

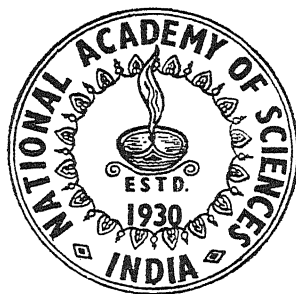
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PROCEEDINGS OF THE NATIONAL ACADEMY OF SCIENCES INDIA

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PART V]

SECTION A

[VOL. XXVII

ON A GENERALIZATION OF LEGENDRE'S POLYNOMIALS

BY K. N. SRIVASTAVA

(*Department of Mathematics, University of Allahabad*)

Received on October 11, 1957

I. INTRODUCTION

ROGRIGUE's formula for Legendre's polynomials¹ led Appell to consider a class of polynomial defined by

$$\frac{d^n}{dx^n} [x^n (1 - x^2)^n]. \quad (1)$$

N. N. Ghosh studied a class of functions defined by²

$$\frac{d^n}{dx^n} \left[x^\mu \left(\frac{1}{x} - x \right)^\nu \right]$$

where μ and ν are any constants. Appell's and Legendre's polynomials are particular cases of these functions. Ghosh also showed that these functions satisfy a differential equation of third order.

In this note we propose to study a class of functions defined by

$$Y = D_k^{nk} [x^\mu (1 - X^k)^\nu]$$

where μ and ν are any constants,

$$k \geq 2. \quad D_k^k = \frac{d}{dx} \cdot \frac{1}{x^{k-2}} \frac{d}{dx}$$

and D_k^{nk} means the operator D_k^k repeated ' n ' times. The above identity includes Ghosh functions, if we take $k = 2$.

2. As a first step in our study, we shall obtain a differential equation satisfied by (1). Let

$$z = x^\mu (1 - x^k)^\nu.$$

or

$$x(1 - x^k) \frac{dz}{dx} + [(\mu + \nu k)x^k - \mu]z = 0.$$

In the above equation replace x by

$$x^{k-1} \cdot \frac{1}{x^{k-2}},$$

and differentiate, divide the expression so obtained by x^{k-2} and differentiate again. Repeating this process $n+1$ times, after some simplification we get a differential equation satisfied by:

$$\begin{aligned} Y &= D_k^{nk} [x^\mu (1 - x^k)^\nu] \\ x^2(1 - x^k) Y''' &+ [4 - k - a + x^k(b - 4)] x Y'' \\ &+ [(k - 2)\{(a - 1) - x^k(b - k - 1)\} \\ &+ x^k\{k(n + 1)(2b + 3k + 1)\}] Y' \\ &+ k(n + 1)(kn + 1)(b + 2nk + k) Y = 0. \end{aligned} \quad (2)$$

3. Let

$$\lambda_{nk, \mu, \nu} = D_k^{nk} [x^\mu (1 - x^k)^\nu].$$

It is easy to see that

$$\lambda_{nk, \mu, \nu} = x^{\mu-kn} (1 - x^k)^{\nu-n} (P_{n,0} + \dots + P_{n,r} x^{rk} + \dots + P_{n,n} x^{nk})$$

where $P_{n,r}$ s are rational integral functions of μ, ν, k and n . Multiplying $\lambda_{nk, \mu, \nu}$ by $x^{kn-\mu} (1 - x^k)^{n-\nu}$ we get a polynomial of degree n in x^k , viz.,

$$\begin{aligned} x^{kn-\mu} (1 - x^k)^{n-\nu} \lambda_{nk, \mu, \nu} &= (P_{n,0} + \dots + P_{n,r} x^{rk} + \dots + P_{n,n} x^{nk}) \\ &= L_{nk, \mu, \nu}. \end{aligned} \quad (3)$$

4. We can write (3) as

$$L_{nk, \mu, \nu} = \lambda_{0, kn-\mu, n-\nu} \cdot \lambda_{nk, \mu, \nu}$$

or

$$\lambda_{nk, \mu, \nu} = \lambda_{0, \mu-kn, \nu-n} \cdot L_{nk, \mu, \nu}. \quad (4)$$

Making this substitution in the differential equation satisfied by $\lambda_{nk, \mu, \nu}$ we get a differential equation satisfied by $L_{nk, \mu, \nu}$.

$$\begin{aligned} x^3(1 - x^k)^3 Z''' &+ x^2(1 - x^k)^2 (A + Bx^k) Z'' \\ &+ x(1 - x^k) (C + Dx^k + Ex^{2k}) Z' \\ &+ (F + Gx^k + Hx^{2k} + Lx^{3k}) = 0 \end{aligned} \quad (5)$$

where

$$A = 3(\mu - kn) + 4 - k - a$$

$$B = b - 4 + 3(\mu - kn)$$

$$C = (\mu - kn)(\mu - kn - 5) + (k - 2)a - 1$$

and similar expressions for D, E, F, G, H and I.

5. From 5 we can evaluate the coefficients $P_{r,r}$ of $L_{nk, \mu, \nu}$ since

$$L_{nk, \mu, \nu} = P_{n,0} + \dots + P_{n,r}x^{rk} + \dots + P_{n,n}x^{nk} \quad (6)$$

substituting in (5) and equating the coefficients of x^{rk} , we get

$$\alpha_\gamma P_{n,r} + \beta_\gamma P_{n,r-1} + \gamma_\gamma P_{n,r-2} + \delta_\gamma P_{n,r-3} = 0 \quad (7)$$

where

$$\begin{aligned} \delta_\gamma = & -(kr - 3k)(kr - 3k - 1)(kr - 3k - 2) \\ & + (kr - 3k)(kr - 3k - 1)B + (kr - 3k)E + I \end{aligned}$$

and similar expressions for α_γ , β_γ and γ_γ .

If we put $r = n + 3$ in (7), we have

$$\delta_{n+3} \cdot P_{n,n} = 0,$$

thus I, E and B satisfy the equation:

$$1 + Ekn + Bkn(kn - 1) - kn(kn - 1)(kn - 2) = 0. \quad (8)$$

By means of above equation we can calculate $P_{n,r}$ in $L_{nk, \mu, \nu}$ starting from $P_{n,0}$ which is known to be

$$\mu(\mu - k + 1)(\mu - k) \dots (\mu - nk + k)(\mu - nk + 1).$$

We may, however, proceed from $P_{n,n}$ and obtain $P_{n,r}$ since

$$P_{n,n} = (-)^n (\mu + vk)(\mu + vk - k + 1) \dots (\mu + vk - nk + 1).$$

6. A hypergeometric expression for $\lambda_{nk, \mu, \nu}$. A simple calculation shows that

$$\lambda_{nk, \mu, \nu} = k^{2n} x^{\mu - kn}.$$

$$\frac{\left[\begin{matrix} (-\nu) \\ (\frac{\mu}{k} + 1) \end{matrix} \right] \left[\begin{matrix} (\frac{\mu + 1}{k}) \\ (\frac{\mu + 1}{k} - n) \end{matrix} \right]}{\left[\begin{matrix} (\frac{\mu}{k} - n) \\ (\frac{\mu + 1}{k} - n) \end{matrix} \right]} {}_3F_2 \left[-\nu, \frac{\mu}{k} + 1, \frac{\mu + 1}{k} \right. \\ \left. \frac{\mu}{k} - n, \frac{\mu + 1}{k} - n; -x^k \right]. \quad (9)$$

7. A class of polynomials is said to form an orthogonal set, if (3, Chapter 2).

$$\int_0^1 \phi_m \phi_n dx = \begin{cases} 0 & \text{for } m \neq n \\ 1 & \text{for } m = n \end{cases} \quad (10)$$

where ϕ_n is a polynomial.

It can be shown that, if

(a) ν is an integer, so that $\lambda_{nk, \mu, \nu}$ is a polynomial,

(b) $\mu + \nu k = 2mk$ or $2nk$ whichever is greater, then by a proper choice of A , the polynomials defined by

$$\phi_n = A \lambda_{nk, \mu, \nu}$$

form an orthogonal set.

I am much indebted to Prof. P. L. Srivastava for his guidance in the preparation of this note. I am also thankful to the Referee for his criticism.

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CHEMICAL SOIL CONDITIONER FOR THE RECLAMATION OF ALKALI SOILS

BY C. L. DHAWAN, M. M. LAL MALHOTRA AND JAGIRSINGH

(Irrigation and Power Research Institute, Amritsar)

Received on May 27, 1958

INCREASING interest is being taken by the Scientists in the use of chemical soil conditioners. Dhawan² reported that a chemical soil conditioner like krilium (0.05-0.1%) could be used for improving the physical structure of barren type of clayey soils at the surface. Ghokhale, Kilee and Narayana⁷ indicated that incorporation of 0.1-0.25% (by weight) of krilium or Poly-ack to 5 lb. samples of screened soil increased water-stable aggregates in medium black soil, lateritic soil and calcareous clay soil (pH > 9) but not in a Na-saturated degraded clay soil. Tamhane and Chibber¹⁴ found that krilium applied at the rate of (0.05-0.1%) on a sandy loam, a loam and a heavy clay were effective as flocculating and aggregate stabilising agents. An increase in aggregation occurred and dispersed Na-Soil.

Faure⁶ reported that krilium markedly increased the number of water-stable aggregates > 0.2 mm. Namise¹¹ showed that krilium increased the number of soil aggregates, the plastic and liquid limits and soil permeability. Balbino¹ came to the conclusion that krilium increased flocculation and sedimentation rates of clay particles. Ramacharlu¹³ presented evidence that evaporation from an alluvial soil decreased with increasing application of conditioners (0.05-1%) krilium. Hernando and Jimeno⁸ opined that in a clay soil receiving N.P.K. at conventional rates, treatment with 0.01-0.05% krilium significantly increased wheat yields in the first year.

Mitsuri, Tensho and Kurihara⁹⁻¹⁰ concluded that application of krilium at low concentration of 0.05-0.2% slightly increased P-fixation. It increased growth, yield and phosphate uptake.

In view of the evidence presented, semi-field experiments were conducted to study the effect of varying percentages of krilium on the amelioration of alkali soils.

Twenty-one small plots measuring 5' x 4' were laid out. The plots were dug 2' deep and requisite percentage of sodium carbonate was added to increase the total soluble salts to about 0.45% in the first foot. The plots were kept fallow for twelve months. Occasional irrigation was applied to make the soil sodium.

The results of analysis of soil, used for this experiment, are given in the table on next page.

Krilium was spread evenly over the plots, ranging from 5-500 lb. per acre. It was thoroughly mixed with the soil.

| Sl. No. | Depth (in inches) | Total soluble salts % | pH |
|---------|----------------------|--------------------------|-------|
| 1 | 0-6 | 0.43 | 10.14 |
| 2 | 6-12 | 0.45 | 10.14 |
| 3 | 12-24 | 0.60 | 10.30 |
| 4 | 24-36 | 0.11 | 8.92 |

Three replications were given to each treatment. On the next day of the addition of kriliium rice seedlings (Jhona 34 a) were transplanted in all the plots. Rice was followed by berseem in winter. Sugarcane was sown in the second year. The varieties of sugarcane tried side by side were Co. 290 and Co. 453.

DISCUSSION OF RESULTS

The average yield of rice per acre in the plots treated with varying percentages of kriliium was as given in Table I.

TABLE I

Average yield of rice/acre (Irrigation 62")

| Sl. No. | Kriliium added per acre (in pounds) | Yield of rice (in pounds/acre) |
|---------|---|-----------------------------------|
| 1 | Control | 278.80 |
| 2 | 5.0 | 278.80 |
| 3 | 10.0 | 278.80 |
| 4 | 50.0 | 278.80 |
| 5 | 100.0 | 309.55 |
| 6 | 250.0 | 278.80 |
| 7 | 500.0 | 278.80 |

The results of Table I showed that there was no effect of kriliium on the yield of rice.

During winter berseem was sown and the total delta applied was 44". The average yield of berseem in the different plots is presented in Table II.

TABLE II
Average yield of berseem (irrigation 44")

| Sl. No. | Krilium added per acre (in pounds) | Average yield of berseem (in pounds/acre × 2178 |
|---------|--|--|
| 1 | Control | 2.16 |
| 2 | 5 | 2.52 |
| 3 | 10 | 3.08 |
| 4 | 50 | 4.36 |
| 5 | 100 | 8.00 |
| 6 | 250 | 8.25 |
| 7 | 500 | 12.81 |

It was inferred from Table II that the yield of berseem only increased in plots treated with krilium at 100 lb. or more than 100 lb. per acre. But its cost is prohibitive at the present rates.

In Table III are enclosed the results of yield of Sugarcane.

TABLE III
Average yield of sugarcane (total irrigation 50")

| Sl. No. | Krilium added per acre (in pounds) | Yield of sugarcane | |
|---------|--|--------------------------------------|---------|
| | | Co. 290 (in pounds/acre × 2178 | Co. 453 |
| 1 | Control | 20.88 | 24.60 |
| 2 | 5 | 24.60 | 24.60 |
| 3 | 10 | 22.93 | 28.70 |
| 4 | 50 | 29.08 | 32.80 |
| 5 | 100 | 38.95 | 35.10 |
| 6 | 250 | 47.53 | 62.53 |
| 7 | 500 | 47.15 | 72.78 |

The yield of sugarcane only increased in plots treated with kriliun at 50 lb. or more than 50 lb. per acre. Apart from the yield the pH value, total soluble salts and dispersion coefficient are the three important factors from which the fertility of a soil can be gauged.

TABLE IV

Comparative values of initial total soluble salts, pH and dispersion coefficient of soils and after rice-berseem (Trifolium alexandrinum) sugarcane rotation

B: Denotes before rice crop;

A: Denotes after sugarcane.

| Sl. No. | Depth | Kriliun [†] added per acre (in pounds) | Total soluble salts | | pH | | Dispersion coefficient | |
|---------|-------|--|------------------------|------|-------|-------|---------------------------|-------|
| | | | B | A | B | A | B | A |
| 1 | 0- 6" | Nil (control) | 0.43 | 0.18 | 10.14 | 10.15 | 91.85 | 83.60 |
| 2 | 6-12" | | 0.45 | 0.28 | 10.14 | 10.30 | 88.52 | 83.22 |
| 3 | 1- 2' | | 0.60 | 0.37 | 10.30 | 10.35 | 90.32 | 85.86 |
| 4 | 2- 3' | | 0.11 | 0.37 | 8.92 | 10.50 | 39.70 | 72.43 |
| 5 | 0- 6" | 5 | 0.43 | 0.28 | 10.14 | 10.13 | 90.32 | 83.72 |
| 6 | 6-12" | | 0.45 | 0.28 | 10.14 | 10.50 | 86.48 | 82.40 |
| 7 | 1- 2' | | 0.60 | 0.37 | 10.30 | 10.32 | 86.52 | 84.88 |
| 8 | 2- 3' | | 0.11 | 0.40 | 8.92 | 10.40 | 40.80 | 71.80 |
| 9 | 0- 6" | 10 | 0.43 | 0.31 | 10.14 | 10.35 | 89.49 | 83.64 |
| 10 | 6-12" | | 0.45 | 0.33 | 10.14 | 10.40 | 86.46 | 83.41 |
| 11 | 1- 2' | | 0.60 | 0.42 | 10.30 | 10.55 | 87.50 | 86.80 |
| 12 | 2- 3' | | 0.11 | 0.47 | 8.92 | 10.50 | 41.20 | 73.42 |
| 13 | 0- 6" | 50 | 0.43 | 0.28 | 10.14 | 10.35 | 92.02 | 86.72 |
| 14 | 6-12" | | 0.45 | 0.28 | 10.14 | 10.40 | 83.27 | 79.82 |
| 15 | 1- 2' | | 0.60 | 0.37 | 10.30 | 10.50 | 86.70 | 85.20 |
| 16 | 2- 3' | | 0.11 | 0.42 | 8.92 | 10.55 | 40.60 | 74.60 |
| 17 | 0- 6" | 100 | 0.43 | 0.21 | 10.14 | 10.00 | 89.55 | 83.72 |
| 18 | 6-12" | | 0.45 | 0.29 | 10.14 | 10.15 | 86.22 | 82.41 |
| 19 | 1- 2' | | 0.60 | 0.37 | 10.30 | 10.20 | 87.53 | 84.40 |
| 20 | 2- 3' | | 0.11 | 0.41 | 8.92 | 10.30 | 41.30 | 73.46 |
| 21 | 0- 6" | 250 | 0.43 | 0.22 | 10.14 | 9.95 | 90.28 | 84.82 |
| 22 | 6-12" | | 0.45 | 0.29 | 10.14 | 10.20 | 85.97 | 92.70 |
| 23 | 1- 2' | | 0.60 | 0.35 | 10.30 | 10.35 | 88.42 | 85.32 |
| 24 | 2- 3' | | 0.11 | 0.42 | 8.92 | 10.30 | 38.30 | 72.42 |
| 25 | 0- 6" | 500 | 0.43 | 0.21 | 10.14 | 9.75 | 91.53 | 84.62 |
| 26 | 6-12" | | 0.45 | 0.28 | 10.14 | 10.00 | 94.64 | 88.74 |
| 27 | 1- 2' | | 0.60 | 0.37 | 10.30 | 10.15 | 92.40 | 86.70 |
| 28 | 2- 3' | | 0.11 | 0.43 | 8.92 | 10.30 | 40.15 | 71.47 |

Dispersion coefficient¹² is the ratio between the percentage of clay on auto-disintegration to the total clay on complete dispersion. The higher the value of dispersion coefficient, the more impeded the movement of water through the soil would be. Dhawan and Sharma³ were of the opinion that the structure of the soil was mainly governed by the dispersion coefficient.

It is well known that structure of a soil is the key to soil fertility. Therefore the dispersion coefficients of the soils of the different plots were determined in order to investigate the effect of krilium on the ultimate fertility of the alkali soils.

Table IV gives the comparative values of total soluble salts, pH and dispersion coefficient of soils before the transplantation of rice seedlings and after the harvesting of sugarcane.

The results given in Table IV left no doubt that an admixture with krilium did not produce any ameliorative effect on the alkaline soils. The structure of the soils, even after three crops, remained in the deteriorated condition as exhibited by the unchanging values of dispersion coefficient. Due to the leaching of sodium carbonate the third foot depth turned highly deteriorated in all the plots. The pH rose from 8.92-10.30 and the dispersion coefficient increased from about 40% to about 72%.

It may also be pointed out that the pH of water solutions at different concentrations of krilium at 25° C. is as follows:

Concentration = 0.1%, 0.5%, 5.0%; pH = 9.6, 9.2, 8.2.

At such high pH values calcium carbonate, usually present in the semi-arid and arid zone soils, cannot be made available for the replacement of Na from the exchange complex. Secondly krilium itself is not a calcium compound.

Summing up the results of the above semi-field experiments, it was concluded that krilium could not be used for the reclamation of alkali soils. Dhawan² had already pointed out from his results of laboratory experiments that only a little improvement in the physical structure of the soil at the surface was possible. But the quantity of krilium needed on one acre plot on the basis of 0.5% comes to about 500 lb. The present cost of this chemical is Rs. 10 per lb. Therefore the cost of krilium at the present rates is prohibitive.

Dhawan and his co-workers have recommended the use of green manuring plants especially Jantar (*Sesbania aculeata*) for the reclamation of alkali soils.⁴⁻⁵

SUMMARY

1. Semi-field experiments were carried out in plots measuring 5' × 4' in which the percentage of krilium ranged from 5 lb. per acre to 500 lb. per acre.
2. The results of the 2 years crop rotations with rice-berseem (*Trifolium alexandrinum*)-sugarcane showed that neither the pH nor the dispersion coefficient were lowered except a little increase in the yield of respective crops in plots, containing krilium more than 50 lb. per acre.
3. Due to the leaching of sodium carbonate from the top layers, even the third foot depth developed deteriorated structure in all the plots on account of the rise in pH and dispersion coefficient.

4. The above results confirmed the previous findings of Dhawan and his co-workers based on laboratory experiments that krilium could not be recommended for the reclamation of alkali soils.

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ON SYMBOLIC CALCULUS OF TWO VARIABLES

BY C. B. L. VARMA

(Department of Mathematics, Mahakoshal Mahavidyalaya, Jabalpur)

Read at the 27th Annual Session of the Academy held at the University of Jabalpur
on 27th December 1957

1. IN the present paper are derived some theorems in symbolic calculus of two variables as developed by McLachlan and Humbert (1949), Voelker and Doetsch (1950), Delerue (1951) and Chakravarti (1953). We shall use the symbolic notation $f(p, q) \doteq h(x, y)$ to represent the convergent double integral

$$\frac{f(p, q)}{pq} = \int_0^\infty \int_0^\infty e^{-ps-ay} h(x, y) dx dy, \quad \begin{matrix} R(p) > 0 \\ R(q) > 0 \end{matrix}$$

In the theorems that follow, we have derived symbolic connections in two variables of the type

$$f\left(\frac{p}{q}\right) \doteq h\left(\frac{x}{y}\right)$$

where h and f are connected by a chain of symbolic relations in one variable. The theorems have been illustrated by suitable examples. The results are believed to be new.

2. THEOREM I.—If

$$f(p) \doteq h(x)$$

and

$$\frac{1}{p^{2\nu-1}} h(p^2) \doteq g(x).$$

Then

$$f\left(\frac{p}{q}\right) \doteq H\left(\frac{x}{y}\right)$$

where

$$H\left(\frac{x}{y}\right) = \sqrt{\frac{2}{\pi}} \cdot \frac{1}{2^\nu} \left(\frac{x}{y}\right)^\nu \int_0^\infty e^{-s^2/8y} D_{2\nu-1}\left(\sqrt{\frac{s^3 x}{2y}}\right) g(s) ds, [\nu > -1].$$

To prove the theorem, we first prove the following lemma:

3. LEMMA.—If we take (3, p.211), the operational representation:

$$\begin{aligned} x^{-\nu} e^{-a/8x} D_{2\nu-1} \sqrt{\frac{a}{2x}} \\ \doteq 2^{\nu-1} \sqrt{\pi} p^\nu e^{-\sqrt{ap}} \end{aligned} \quad \begin{matrix} [R(p) > 0] \\ [R(a) > 0] \end{matrix}$$

$$\begin{aligned}
& \doteq \frac{1}{2p} 2^{\nu+1} \sqrt{\pi} p^{\nu+1} e^{-\sqrt{ap}} \\
& = \frac{1}{2} \int_0^{\infty} x^{-\nu-1} e^{-a/8x} D_{2\nu+1} \left(\sqrt{\frac{a}{2x}} \right) dx \\
& = \frac{1}{2} \int_0^{\infty} H(t) dt, \text{ say.}
\end{aligned} \tag{3.1}$$

Now, (Chakravarti, p. 240),

$$\int_0^{y/x} H(t) dt \doteq p \int_0^{\infty} \frac{H(t)}{p+qt} dt. \tag{3.2}$$

Hence we get

$$\begin{aligned}
& 2 \left(\frac{y}{x} \right)^{-\nu} e^{-ay/8y} D_{2\nu-1} \left(\sqrt{\frac{ax}{2y}} \right) \\
& \doteq p \int_0^{\infty} \frac{x^{-\nu-1} e^{-a/8x} D_{2\nu+1} \left(\sqrt{\frac{a}{2x}} \right) dx}{p+qx} \\
& \doteq p \int_0^{\infty} \frac{2^{\nu+1} y^{\nu} e^{-ay/4} D_{2\nu+1} (\sqrt{ay}) dy}{2py+q}.
\end{aligned} \tag{3.3}$$

To evaluate the integral on the right, we have (2, p. 121)

$$\begin{aligned}
& \int_0^{\infty} D_{\nu}(y) e^{-\frac{1}{2}y^2} y^{\nu} (x^2 + y^2)^{-1} dy \\
& = \sqrt{\frac{\pi}{2}} \Gamma(\nu+1) x^{\nu-1} e^{\frac{1}{2}x^2} D_{-\nu-1}(x), \quad [\nu > -1].
\end{aligned}$$

Changing ν into $2\nu+1$ and putting $x^2 = \xi$ and $y^2 = a\eta$, we get,

$$\begin{aligned}
& \int_0^{\infty} \eta^{\nu} \frac{D_{2\nu+1}(\sqrt{a\eta}) e^{-\frac{1}{2}a\eta}}{\xi + a\eta} d\eta \\
& = \frac{\sqrt{2\pi} \cdot \Gamma(2\nu+2)}{a^{\nu+1}} e^{\frac{1}{2}\xi} D_{-2\nu-2}(\sqrt{\xi}) \xi^{\nu}, \quad [\nu > -1]
\end{aligned}$$

Taking

$$\xi = \frac{aq}{2p} \quad \text{and} \quad \eta = y$$

$$\begin{aligned} & \int_0^\infty \frac{y^\nu e^{-ay/4} D_{2\nu+1}(\sqrt{ay}) dy}{2py + q} \\ &= \frac{\sqrt{2\pi} \Gamma(2\nu + 2)}{2^{\nu+1}} \cdot \frac{q^\nu}{p^{\nu+1}} \cdot e^{aq/8p} D_{-2\nu-2} \left(\sqrt{\frac{aq}{2p}} \right). \end{aligned} \quad (3.4)$$

Substituting this value in (3.3)

$$\begin{aligned} & \left(\frac{y}{x} \right)^{-\nu} e^{-as/8y} D_{2\nu-1} \left(\sqrt{\frac{ax}{2y}} \right) \\ & \doteq \sqrt{\frac{\pi}{2}} \cdot \Gamma(2\nu + 2) \cdot \left(\frac{q}{p} \right)^\nu e^{aq/8p} D_{-2\nu-2} \left(\sqrt{\frac{aq}{2p}} \right). \end{aligned}$$

4. To prove the theorem now, we have (Shastri, p. 4),

If

$$f(p) \doteq h(x)$$

and

$$p^{m+3}h(p^2) \doteq g(x),$$

then

$$f(p) = \Gamma(-m) (2p)^{m/2+1} \int_0^\infty e^{s^2/8p} D_m \left(\frac{s}{\sqrt{2p}} \right) g(s) ds \quad \text{R}(m) < 0.$$

Putting $m = -2\nu - 2$ and changing p into p/q ,

$$f\left(\frac{p}{q}\right) = \Gamma(2\nu + 2) \left(\frac{2p}{q}\right)^{-\nu} \int_0^\infty e^{s^2 q/8p} D_{-2\nu-2} \left(\sqrt{\frac{s^2 q}{2p}} \right) g(s) ds$$

[$\nu > -1$]

using (3.5) and interpreting by

$$\begin{aligned} & \left(\frac{y}{x} \right)^{-\nu} e^{-s^2 q/8y} D_{2\nu-1} \left(\sqrt{\frac{s^2 x}{2y}} \right) \\ & \doteq \sqrt{\frac{\pi}{2}} \left(\frac{q}{p} \right)^\nu \Gamma(2\nu + 2) e^{s^2 q/8p} D_{-2\nu-2} \left(\sqrt{\frac{s^2 q}{2p}} \right) \quad [\nu > -1]. \end{aligned}$$

we get the theorem.

Example 1.—As an application of the theorem, let

$$g(x) \equiv \frac{x^n \cdot \sqrt{\pi} \cdot J_{n-1}(x)}{2^n \Gamma(n + \frac{1}{2})} \doteq \frac{p^2}{(1 + p^2)^{n+\frac{1}{2}}} = \frac{1}{p^{2\nu-1}} h(p^2)$$

$$\therefore h(x) = \frac{x^{\nu+\frac{1}{2}}}{(1+x)^{n+\frac{1}{2}}} \doteq \Gamma\left(\nu + \frac{3}{2}\right) p^{\frac{1}{2}(n-\nu)} e^{\frac{1}{2}p} W_{-\frac{1}{2}(\nu+n+1), \frac{1}{2}(\nu-n+1)}(p)$$

$$\doteq f(p).$$

The theorem then gives

$$(i) \quad f\left(\frac{p}{q}\right) \equiv \Gamma\left(\nu + \frac{3}{2}\right) \left(\frac{p}{q}\right)^{\frac{1}{2}(n-\nu)} e^{p/2q} W_{-\frac{1}{2}(\nu+n+1), \frac{1}{2}(\nu-n+1)}\left(\frac{p}{q}\right)$$

$$\doteq \sqrt{\frac{2}{\pi}} \cdot \frac{1}{2^\nu} \left(\frac{x}{y}\right)^\nu \int_0^\infty e^{-s^2 s/8y} D_{2\nu-1}\left(\sqrt{\frac{s^2 x}{2y}}\right)$$

$$\times \frac{s^n \cdot \sqrt{\pi} J_{n-1}(s)}{2^n \Gamma(n + \frac{1}{2})} \cdot ds.$$

Evaluating the integral on the right by (Shastri, p. 8),

$$\int_0^\infty e^{s^2/8p} s^n J_{n-1}(s) D_{-2m}\left(\frac{s}{\sqrt{2p}}\right) ds$$

$$= \frac{\Gamma(n + \frac{1}{2})}{\Gamma(m)} 2^{n-m} p^{\frac{1}{2}(n+m-1)} e^{\frac{1}{2}p} W_{-\frac{1}{2}(n+m), -\frac{1}{2}(n-m)}(p)$$

$$R(n) > 0$$

$$R(m) > 0$$

in which changing p into y/x and m into $\frac{1}{2} - \nu$ we get after substituting in (i):

$$\Gamma\left(\nu + \frac{3}{2}\right) \left(\frac{p}{q}\right)^{\frac{1}{2}(n-\nu)} e^{p/2q} W_{-\frac{1}{2}(\nu+n+1), \frac{1}{2}(\nu-n+1)}\left(\frac{p}{q}\right)$$

$$\doteq \frac{1}{\Gamma(\frac{1}{2} - \nu)} e^{y/2x} \left(\frac{y}{x}\right)^{\frac{1}{2}(n-3\nu-\frac{1}{2})} W_{-\frac{1}{2}(n-\nu+\frac{1}{2}), -\frac{1}{2}(n+\nu-\frac{1}{2})}\left(\frac{y}{x}\right)$$

$$[\nu < \frac{1}{2}].$$

Example 2.—Taking

$$g(x) \equiv \frac{x^n J_n(x) \sqrt{\pi}}{2^n \Gamma(n + \frac{1}{2})} \doteq \frac{p}{(1 + p^2)^{n+\frac{1}{2}}} = \frac{1}{p^{2\nu-1}} h(p^2)$$

$$\therefore h(x) = \frac{x^\nu}{(1+x)^{n+\frac{1}{2}}} \doteq \Gamma(\nu + 1) e^{\frac{1}{2}p} p^{-\frac{1}{2}(\nu-n-\frac{1}{2})}$$

$$\times W_{-\frac{1}{2}(n+\nu+\frac{1}{2}), \frac{1}{2}(\nu-n+\frac{1}{2})}(p)$$

$$\doteq f(p).$$

The theorem then gives

$$f\left(\frac{p}{q}\right) = \Gamma(\nu + 1) e^{p/2q} \left(\frac{p}{q}\right)^{-\frac{1}{2}(\nu-n+\frac{1}{2})} W_{-\frac{1}{2}(\nu+n+\frac{1}{2}), \frac{1}{2}(\nu-n+\frac{1}{2})}\left(\frac{p}{q}\right) \\ \doteq \sqrt{\frac{2}{\pi}} \cdot \frac{1}{2^\nu} \left(\frac{x}{y}\right)^\nu \int_0^\infty e^{-s^2/8y} D_{2\nu-1}\left(\sqrt{\frac{s^2x}{2y}}\right) \frac{s^n J_n(s)}{2^n \Gamma(n+\frac{1}{2})} \sqrt{\pi} \cdot ds.$$

The integral on the right can be evaluated by (Shastri, 1945)

$$\int_0^\infty e^{s^2/8p} s^n J_n(s) D_{-2m}\left(\frac{s}{\sqrt{2p}}\right) ds \\ = \frac{\Gamma(n+\frac{1}{2})}{\Gamma(m+\frac{1}{2})} 2^{n-m} p^{\frac{1}{2}(n+m-\frac{1}{2})} e^{\frac{1}{2}p} W_{-\frac{1}{2}(n+m-\frac{1}{2}), \frac{1}{2}(n-m+\frac{1}{2})}(p), \\ R(n) > -\frac{1}{2}, R(m) > 0$$

so that

$$\Gamma(\nu + 1) e^{p/2q} \left(\frac{p}{q}\right)^{-\frac{1}{2}(\nu-n+\frac{1}{2})} W_{-\frac{1}{2}(\nu+n+\frac{1}{2}), \frac{1}{2}(\nu-n+\frac{1}{2})}\left(\frac{p}{q}\right) \\ \doteq \frac{1}{\Gamma(1-\nu)} e^{p/2q} \left(\frac{y}{x}\right)^{\frac{1}{2}(n-3\nu)} W_{-\frac{1}{2}(n-\nu), \frac{1}{2}(n+\nu)}\left(\frac{y}{x}\right), \quad [\nu < 1].$$

5. THEOREM II.—(i) If

$$(i) \quad f(x) \doteq h(p)$$

and

$$(ii) \quad p^\nu h(\sqrt{p}) \doteq H(x)$$

then

$$H\left(\frac{y}{x}\right) \doteq F\left(\frac{q}{p}\right)$$

where

$$F\left(\frac{q}{p}\right) = \frac{\Gamma(2\nu+2)}{2^\nu} \left(\frac{q}{p}\right)^\nu \int_0^\infty e^{s^2 q/8p} D_{-2\nu-2}\left(\sqrt{\frac{s^2 q}{2p}}\right) f(s) ds \\ [\nu > -1].$$

Proof.—We have by (i) and (ii) above (3, p. 133),

$$H(x) = \frac{x^{-\nu}}{2^{\nu-\frac{1}{2}} \sqrt{\pi}} \cdot \int_0^\infty e^{-u^2/8x} D_{2\nu-1}\left(\frac{u}{\sqrt{2x}}\right) f(u) du.$$

Changing x into y/x and interpreting by (3.5), i.e.,

$$\left(\frac{x}{y}\right)^{\nu} e^{-u^2 a/8y} D_{2\nu-1} \left(\sqrt{\frac{u^2 x}{2y}}\right) \\ \doteq \sqrt{\frac{\pi}{2}} \cdot \left(\frac{q}{p}\right)^{\nu} \Gamma(2\nu+2) e^{u^2 a/8p} D_{-2\nu-2} \left(\sqrt{\frac{u^2 q}{2p}}\right) \quad [\nu > -1]$$

we get the theorem.

Example.—Taking

$$f(x) \equiv x^{\nu+1} J_{\nu+1}(ax)$$

we have

$$h(p) = \frac{(2a)^{\nu+1}}{\sqrt{\pi}} \Gamma\left(\nu + \frac{3}{2}\right) p (p^2 + a^2)^{-\nu-3/2} \\ \therefore p^{\nu} h(\sqrt{p}) = \frac{(2a)^{\nu+1}}{\sqrt{\pi}} \Gamma\left(\nu + \frac{3}{2}\right) p^{\nu+1/2} (p + a^2)^{-\nu-3/2} \\ \doteq H(x).$$

Then

$$H\left(\frac{y}{x}\right) \doteq \frac{\Gamma(2\nu+2)}{2^{\nu}} \left(\frac{q}{p}\right)^{\nu} \int_0^{\infty} e^{s^2 a/8p} \\ \times D_{-2\nu-2} \left(\sqrt{\frac{s^2 q}{2p}}\right) s^{\nu+1} J_{\nu+1}(as) ds \quad [\nu > -1].$$

The integral on the right can be evaluated by using the result (2, p. 121)

$$\int_0^{\infty} (xy)^{\frac{1}{2}} J_{\nu}(xy) y^{\nu-1/2} e^{t^2 y^2} D_{-2\nu}(y) dy \\ = x^{\nu-1/2} e^{t^2 x^2} D_{-2\nu}(x) \quad [\nu > -\frac{1}{2}].$$

Changing ν into $\nu+1$ so that $\nu > -3/2$ and putting

$$y = \sqrt{\frac{q}{2p}} \cdot s$$

and

$$x = a \sqrt{\frac{2p}{q}}$$

we get

$$\int_0^{\infty} s^{\nu+1} J_{\nu+1}(as) e^{s^2 a/8p} D_{-2\nu-2} \left(\sqrt{\frac{s^2 q}{2p}}\right) ds \\ = a^{\nu} \left(\frac{2p}{q}\right)^{\nu+1} e^{a^2 p/2q} D_{-2\nu-2} \left(\sqrt{\frac{2a^2 p}{q}}\right)$$

so that

$$\begin{aligned} H\left(\frac{y}{x}\right) &\doteq \Gamma(2\nu + 2) \cdot \frac{2p}{q} e^{a^2\nu/2a} D_{-2\nu-2} \left(\sqrt{\frac{2a^2p}{q}} \right) \\ &\doteq F\left(\frac{p}{q}\right). \quad [\nu > -1]. \end{aligned}$$

Particular case: taking $\nu = \frac{1}{2} [> -1]$, we have

$$\begin{aligned} p^{\nu} h(\sqrt{p}) &= \frac{(2a)^{3/2}}{\sqrt{\pi}} \frac{p}{(p+a^2)^2} \doteq \frac{(2a)^{3/2}}{\sqrt{\pi}} x e^{-a^2x} = H(x) \\ \therefore a^{3/2} \left(\frac{y}{x}\right) e^{-a^2y/2} &\doteq \sqrt{2\pi} \left(\frac{p}{q}\right) e^{a^2\nu/2a} D_{-3} \left(\sqrt{\frac{2a^2p}{q}} \right). \end{aligned}$$

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RECLAMATION OF ALKALI SOILS BY DIFFERENT CROP ROTATIONS

BY C. L. DHAWAN, B. B. L. BHATNAGAR, TARA SINGH,
PUSHAP DEV AND MANGAL SINGH

(Irrigation and Power Research Institute, Punjab, Amritsar)

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DHAWAN and his associates^{1,2} arrived at the following conclusions from their experiments conducted in the laboratory and semi-field scale for the reclamation of alkali soils.

(1) Molasses alone cannot be used successfully for the reclamation of black alkali soils. Molasses in combination with lime-sludge (another waste product from sugar factories) can be employed efficiently for the reclamation of such type of soils.

(2) Distillery waste (a waste product from alcohol factories) is very effective in reducing alkalinity, provided the transport charges are within an economical reach.

(3) Sulphuric acid, gypsum and calcium chloride are quite promising in the reclamation of alkali soils, but the cost of sulphuric acid is prohibitive.

(4) Green manuring may also be employed for ameliorating these soils, but the effect is a slow one.

(5) A rotation of sugarcane mars the alkalinity of the soil to a great extent. But the water-logged conditions do not respond very successfully to such rotations due to bad aeration coupled with deteriorated structure of the soil in the presence of sodium carbonate.

(6) For the reclamation of water-logged black alkali soils, suitable crop rotations with some suitable cheap reclaiming agent seem to be necessary.

(7) Jantar (*Sesbania aculeata*) root system may be used as a field method for determining the suitability of a particular treatment for the reclamation of black alkali soils.

It is an accepted fact that the reclamation of alkali soils is beset with great difficulty as it involves not only leaching soluble salts but also neutralising excess alkalinity, replacing exchangeable sodium by calcium and improving the structure of the soil.

In Hungary Desigmond³ reclaimed the alkali soils locally known as "Szik" by providing (a) drainage, (b) preventing the upward movement of salts by surface mulches or by cultivating alfalfa and (c) making the hard pan pervious by adding either pressed lime from sugar factories, gypsum, calcium carbonate and farm manure.

The question of the cost and easy availability of a reclaiming agent is sometimes a great bottle-neck. It was, therefore, desired to investigate some form of

suitable crop rotation without the use of any reclaiming agent for the amelioration of such type of soils.

EXPERIMENTAL

An area of 52' × 24' containing high percentage of sodium carbonate and sodium bicarbonate was selected and divided into eight sub-plots A, A₁, B, B₁, C, C₁, D, D₁ each of 24' × 5'. The initial salt content and alkalinity of all the sub-plots were high throughout the depth of the soil profiles (Figs. 1-8). The percentage of the different salts in the various sub-plots is given in Table I. Water-table existed between 8'-9'.

The following crop rotations were carried out:

| Sl. No. | Sub-Plot | Rotation |
|---------|--------------------|---|
| 1 | A & A ₁ | Leaching-jantar (<i>Sesbania aculeata</i>)—Fallow-jantar (green-manuring). |
| 2 | B & B ₁ | Sugarcane—ratooned. |
| 3 | C & C ₁ | Leaching-rice-gram. |
| 4 | D & D ₁ | Leaching-swank (<i>Panicum colonum</i>)—Berseem (<i>Trifolium alexandrinum</i>) |

DATA AND DISCUSSION

From a practical view-point, total soluble salts and pH are the principal factors controlling the salinity-cum-alkalinity of a soil.^{4, 9} But the deterioration of an alkali soil is also proportional to the extent to which sodium has replaced the divalent bases in the soils, *i.e.*, how far alkalisiation has proceeded. Puri⁵ has defined the degree of alkalisiation of soil as the ratio of the amount of exchangeable monovalent ions (Na plus K) in the soil (*n*) to the maximum amount of monovalent ions the soil is capable of binding by exhaustive treatment with a neutral salt (*N*).

$$\text{Degree of alkalisiation} = 100 \times \frac{n}{N}.$$

According to Puri⁵ for soils with degree of alkalisiation less than 25% crop yields would not be affected, between 25-75% there was an inverse linear relationship between that characteristic and yield and beyond 75% the crop yield would be greatly diminished.

The soil samples were analysed for total soluble salts, pH and exchangeable bases.⁶⁻⁷

In general, salt content had been considerably reduced in all the sub-plots (Figs. 1-8). The behaviour of alkalinity and exchangeable bases is different under different rotations which are discussed below:

I. Sub-Plots A and A₁

Rotation.—Leaching-jantar (*Sesbania aculeata*)-fallow-jantar green manuring.

The total delta applied was 61.5" during first year Kharif, out of which 39.5" were used for leaching. After leaching, jantar (*Sesbania aculeata*) was sown. The plots remained fallow in winter and during next Kharif, jantar (*Sesbania aculeata*) was buried as green manure during the month of August, when it had attained the desirable height (10,880 kilograms per acre).

The reclamation operations resulted appreciably in the reduction of salts (Figs. 1 and 2) but the pH only decreased substantially in plot A₁ upto 5' depth as compared with plot A. The reason is not far to seek. The percentage of total soluble salt was very high in plot A (1.58% from 0-6"), while in plot A₁ it was 0.34% (from 0-6"). The predominant salt in both the profiles was sodium bicarbonate. On leaching, the liberated sodium ions replaced the exchangeable calcium and, therefore, the pH in first year Kharif increased in both the profiles A and A₁ (Figs. 1 and 2), when jantar (*Sesbania aculeata*) was buried, the pH began to fall, due to the formation of complex organic acids which lowered the pH value. The organic acids produced from jantar decreased the high pH even up to 5th foot depth. This effect was comparatively smaller in plot A, as the leached-out sodium bicarbonate from the top layers (0.79% from 0-6" in plot A) did not allow the calcium ions to compete successfully with the monovalent sodium ions for positions in the exchange complex, though there was a lowering in pH value up to 5th foot depth. The results of degree of alkalisiation (Table II) further lend support to the above conclusions.

TABLE II

Showing the results of degree of alkalisiation in sub-plots A and A₁ before and after jantar green manuring

(After five crop seasons)

| Depth (in ft.) | Degree of alkalisiation | | | |
|-------------------|-------------------------|-------|-------------------------|-------|
| | Sub-Plot A | | Sub-Plot A ₁ | |
| | Initial | Final | Initial | Final |
| 0-0.5 | 88.7 | 66.0 | 48.3 | 24.5 |
| 0.5-1.0 | 77.2 | 70.0 | 49.3 | 30.0 |
| 1.0-2.0 | 90.5 | 66.1 | 53.5 | 39.9 |
| 2.0-3.0 | 89.0 | 55.3 | 46.6 | 26.3 |
| 3.0-4.0 | 90.8 | 58.0 | 50.7 | 35.5 |
| 4.0-5.0 | 61.8 | 63.1 | 42.4 | 31.1 |
| 5.0-6.0 | 60.0 | 64.0 | 40.6 | 32.0 |
| 6.0-7.0 | 46.7 | 63.1 | 41.3 | 31.9 |
| 7.0-8.0 | 45.0 | 50.9 | 30.9 | 27.8 |

Sub-Plot A

FIG. 1

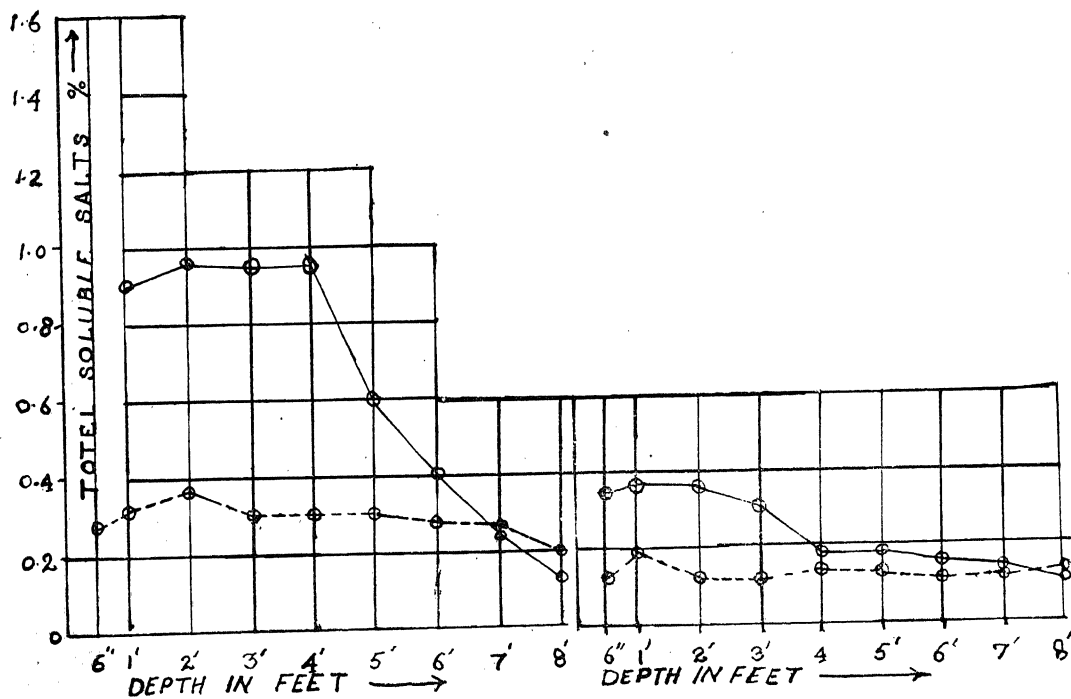
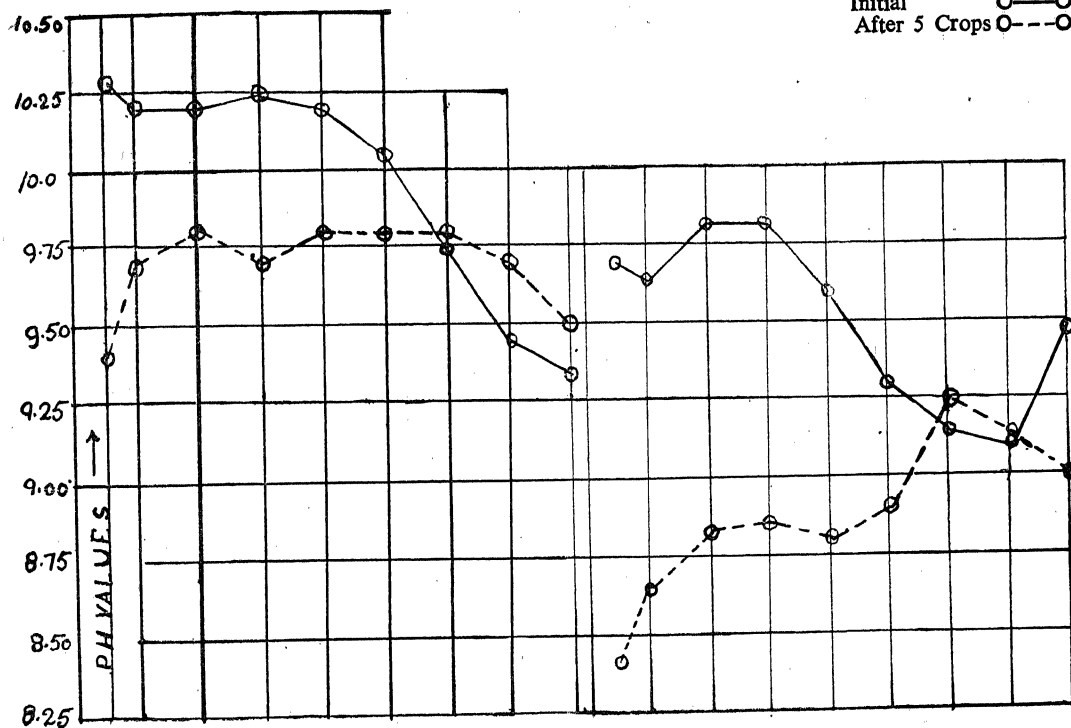
Sub-Plot A₁

FIG. 2

FIGS. 1 and 2. Effect of Jantar (*Sesbania aculeata*) on the alkalinity and total soluble salts of alkali soils.

In such cases where the soils are infested with a high percentage of sodium carbonate or sodium bicarbonate green manuring may have to be resorted to more than two times, as its effect is a slow one. The presence of sodium carbonate makes the soils impervious, which is responsible for the slow action of the reclaiming agents.

II. Sub-Plots B and B₁

In this case no leaching was done and the sugarcane crop utilised a total delta of nearly 53" every year. The condition of the crop was quite satisfactory. This rotation decreased total soluble salts even upto 8' depth. But the alkalinity was not reduced except in the top first foot (Figs. 3 and 4) even after third year Kharif.

The pH had increased appreciably in plot B (Fig. 3) below 3rd foot due to the washed out sodium bicarbonate from the upper layers removing the exchangeable calcium and thus increasing the degree of alkalisation and pH. The results of degree of alkalisation given in Table III confirm the above findings.

A glance at the Table III shows that the degree of alkalisation has either remained practically same or has increased at lower depth (which is quite possible) due to the released sodium ions removing the equivalent exchangeable calcium from the soil.

Two important conclusions emerge out of the above investigation.

(i) Sugarcane can stand a sufficiently high degree of alkalinity.

(ii) It is not very conducive in reducing the alkalinity of the alkali soil as is the case with the rice plants which liberate carbon dioxide from its roots, whose pH being about 4.0,⁸ assists in lowering the high alkalinity. Such reactions do not occur in sugarcane. Therefore this rotation does not help very much in decreasing the alkalinity of the soil.

III. Sub-Plots C and C₁

These plots were subjected to 18.5" leaching in the beginning and were then put under rice. The rice was matured on a delta of 30". An improvement in the shape of reduction of only salt content had been affected.

Rice was followed by gram and was finally green-manured by guara (*Gyamopsis-psoralioides*) after one and two years of the above rotations, the same rotation of rice and gram was tried. Though there was no reduction in alkalinity except in the top 3' (Figs. 5 and 6), yet this rotation behaved better than sugarcane.

This shows that even rice coupled with gram and green-manured with guara (*Gyamopsis-psoralioides*) does not break easily the deteriorated structure of the black alkali soils. But jantar (*Sesbania aculeata*) green manuring, as was discussed under plots A and A₁ above was much more effective in bringing down the alkalinity even at lower depths. The results of degree of alkalisation given in Table IV also support the above conclusions. The degree of alkalisation either remained the same or had increased a little below 2½' depth, as was the case with sugarcane.

Sub-Plot B

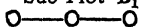
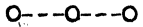
Initial  Sub-Plot B₁
After 5 Crops 

FIG. 3

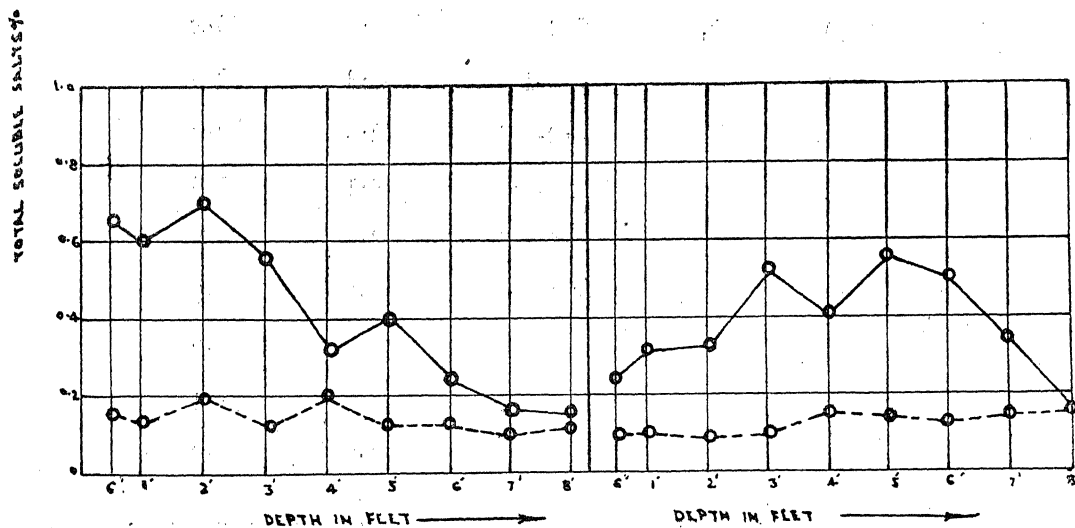
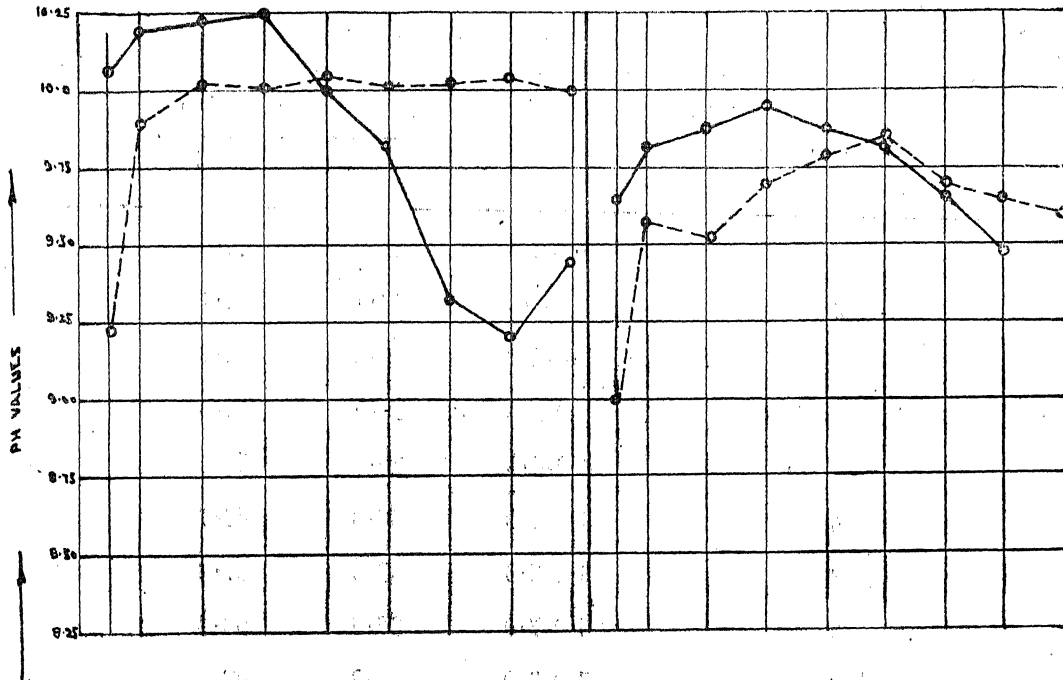


FIG. 4

Figs. 3 and 4. Effect of sugarcane rotation on the alkalinity and total salts of alkali soil,

TABLE III

Comparison of degree of alkalisation before and after reclamation operation in sub-plots B and B₁

(After five crop seasons)

| Sl. No. | Sub-Plot No. | Depth (in feet) | Degree of alkalisation | |
|---------|----------------|--------------------|------------------------|-------|
| | | | Initial | Final |
| 1 | B | 0.0-0.5 | 63.9 | 40.0 |
| 2 | | 0.5-1.0 | 63.1 | 58.1 |
| 3 | | 1.0-2.0 | 55.6 | 58.3 |
| 4 | | 2.0-3.0 | 58.2 | 60.5 |
| 5 | | 3.0-4.0 | 79.9 | 66.6 |
| 6 | | 4.0-5.0 | 67.0 | 68.7 |
| 7 | | 5.0-6.0 | 37.6 | 67.8 |
| 8 | | 6.0-7.0 | 35.5 | 58.4 |
| 9 | | 7.0-8.0 | 54.2 | 42.4 |
| 10 | B ₁ | 0.0-0.5 | 49.5 | 30.2 |
| 11 | | 0.5-1.0 | 52.3 | 50.0 |
| 12 | | 1.0-2.0 | 42.6 | 50.0 |
| 13 | | 2.0-3.0 | 49.1 | 47.5 |
| 14 | | 3.0-4.0 | 54.6 | 45.9 |
| 15 | | 4.0-5.0 | 56.0 | 47.7 |
| 16 | | 5.0-6.0 | 50.0 | 52.2 |
| 17 | | 6.0-7.0 | 52.8 | 48.1 |
| 18 | | 7.0-8.0 | 35.2 | 51.2 |

plots. But its ameliorative power for the reclamation of alkali soils is better than sugarcane.

Sub-Plot C

FIG. 5

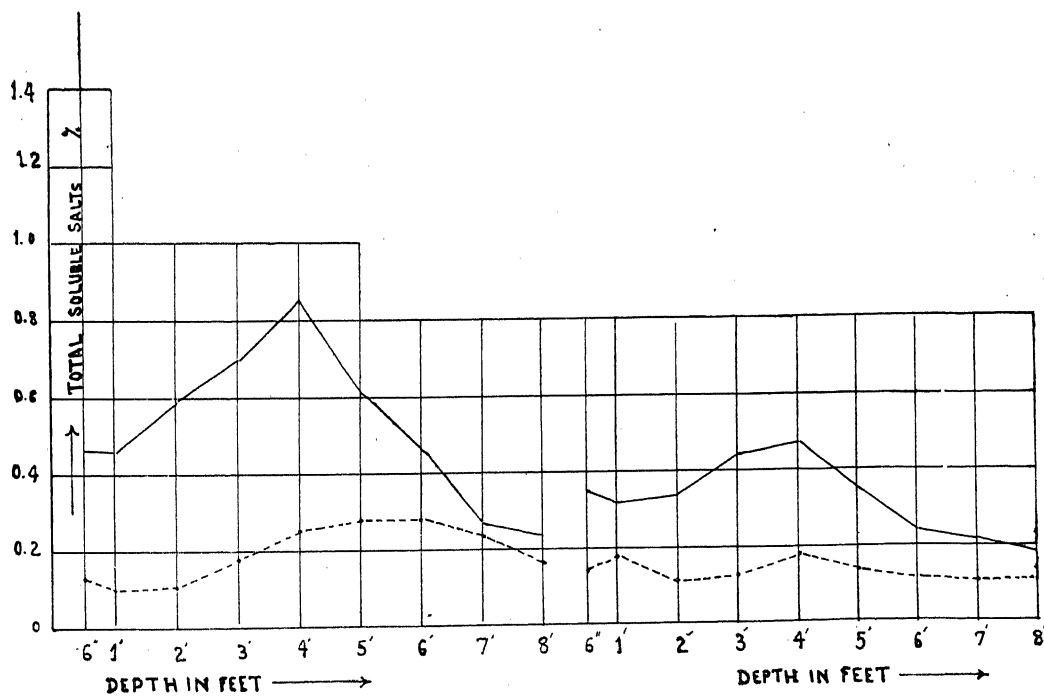
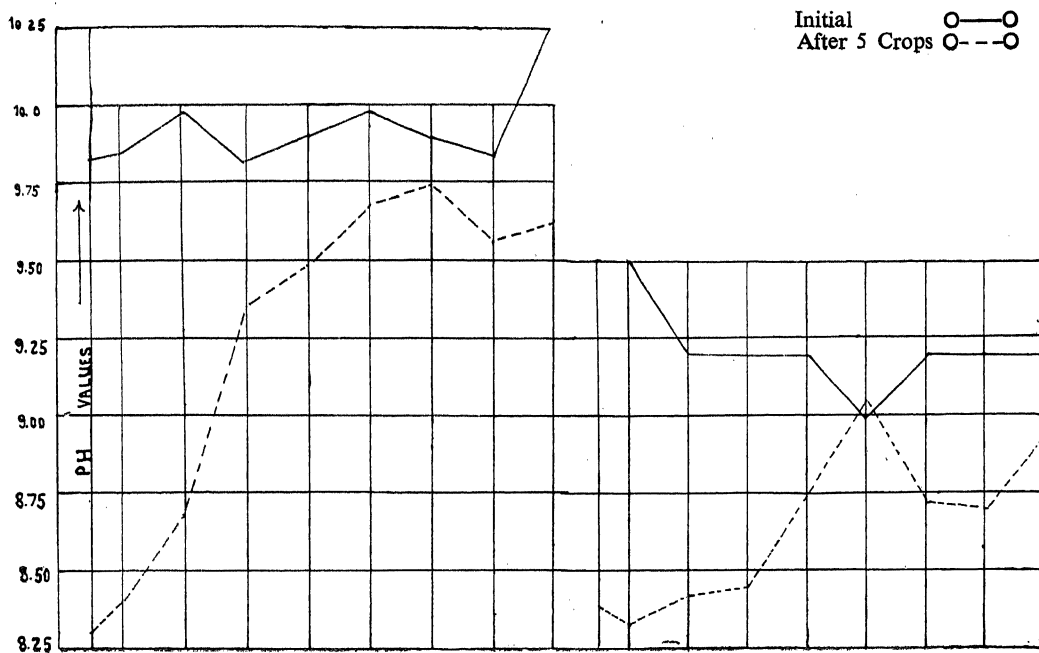
Sub-Plot C₁

FIG. 6

Figs. 5 and 6. Effect of leaching-rice-gram rotation on the alkalinity and total soluble salts of alkali soil.

TABLE IV

Comparison of degree of alkalisation before and after reclamation operation in sub-plots C and C₁

(After five crop seasons)

| Sl. No. | Sub-Plot No. | Depth (in feet) | Degree of alkalisation | |
|---------|----------------|--------------------|------------------------|-------|
| | | | Initial | Final |
| 1 | C | 0.0-0.5 | 53.9 | 22.0 |
| 2 | | 0.5-1.0 | 53.9 | 28.8 |
| 3 | | 1.0-2.0 | 67.6 | 29.9 |
| 4 | | 2.0-3.0 | 59.2 | 48.1 |
| 5 | | 3.0-4.0 | 67.2 | 60.7 |
| 6 | | 4.0-5.0 | 54.5 | 62.1 |
| 7 | | 5.0-6.0 | 56.3 | 57.1 |
| 8 | | 6.0-7.0 | 44.1 | 52.1 |
| 9 | | 7.0-8.0 | 50.0 | 47.5 |
| 10 | C ₁ | 0.0-0.5 | 56.3 | 25.0 |
| 11 | | 0.5-1.0 | 58.5 | 39.8 |
| 12 | | 1.0-2.0 | 49.2 | 44.0 |
| 13 | | 2.0-3.0 | 51.6 | 38.8 |
| 14 | | 3.0-4.0 | 68.9 | 49.6 |
| 15 | | 4.0-5.0 | 47.1 | 50.7 |
| 16 | | 5.0-6.0 | 40.2 | 45.1 |
| 17 | | 6.0-7.0 | 33.9 | 34.5 |
| 18 | | 7.0-8.0 | 40.4 | 36.1 |

IV. Sub-Plots D and D₁

Here the rotation was Leaching-Swank (*Panicum colonum*) Berseem (*Trifolium alexandrinum*)-Leaching-Swank-Berseem-leaching-Swank-Berseem.

Sub-Plot D

FIG. 7

Sub-Plot—D₁

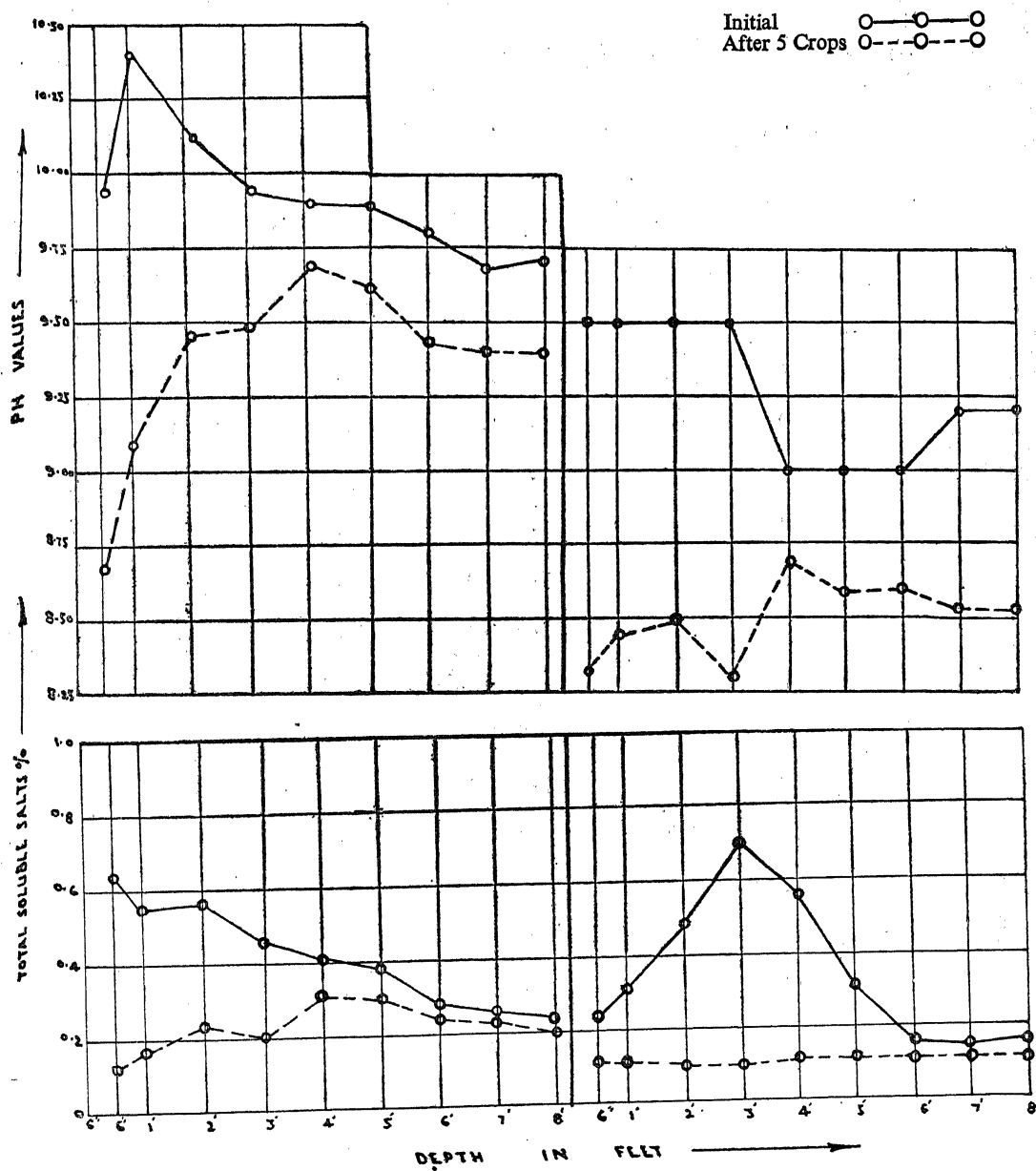


FIG. 8

FIGS. 7 and 8. Effect of swank-berseem rotation on the alkalinity and total soluble salts of alkali soils.

The total delta applied every year was 62", out of which 23" were used for leaching. Analyses indicated that the salts had decreased substantially upto 8' depth. Significant reduction in pH was not noticeable in plot D (Figs. 7 and 8). The plot D was in a very highly deteriorated condition as compared with plot D₁. The initial pH in plot D was not less than 9.6 even upto 8' depth (Fig. 7).

TABLE V

Showing the results of degree of alkalisiation in sub-plots D and D₁
(Before and after five crop seasons)

| Sl. No. | Sub-Plot No. | Depth (in feet) | Degree of alkalisiation | |
|---------|----------------|--------------------|-------------------------|-------|
| | | | Initial | Final |
| 1 | D | 0.0-0.5 | 83.1 | 39.8 |
| 2 | | 0.5-1.0 | 81.6 | 53.3 |
| 3 | | 1.0-2.0 | 75.1 | 55.5 |
| 4 | | 2.0-3.0 | 82.4 | 54.9 |
| 5 | | 3.0-4.0 | 93.7 | 71.2 |
| 6 | | 4.0-5.0 | 72.9 | 57.1 |
| 7 | | 5.0-6.0 | 63.2 | 45.1 |
| 8 | | 6.0-7.0 | 71.4 | 43.5 |
| 9 | | 7.0-8.0 | 75.6 | 51.5 |
| 10 | D ₁ | 0.0-0.5 | 53.0 | 38.9 |
| 11 | | 0.5-1.0 | 59.9 | 27.3 |
| 12 | | 1.0-2.0 | 65.3 | 33.3 |
| 13 | | 2.0-3.0 | 73.0 | 25.0 |
| 14 | | 3.0-4.0 | 61.5 | 28.5 |
| 15 | | 4.0-5.0 | 40.6 | 29.0 |
| 16 | | 5.0-6.0 | 55.5 | 34.4 |
| 17 | | 6.0-7.0 | 46.1 | 34.6 |
| 18 | | 7.0-8.0 | 44.2 | 38.7 |

The initial pH from 6-12" depths was 10.4 and 9.6 upto 8' depth. But in plot D₁, the highest initial pH was only 9.5.

Judging these plots from the point of view of standards investigated by Taylor,⁹ who considered soils below 8.5 pH value and 0.2% total soluble salt content as normal the plot D₁ had been reclaimed upto 3' depth completely, while the plot D was still in a deteriorated condition. It needed further reclamation operation. The results of alkalisations for these sub-plots as embodied in Table V also pointed to the same conclusions that the plot D₁ being very highly deteriorated could not be reclaimed to the same degree as plot D₁. The degree of alkalisations in plot D₁ had been reduced even upto 8' depth.

TABLE VI
Showing the detailed analysis of initial sampling

| Sub-Plot No. | Depth (in feet) | pH | Total soluble salt % | Na ₂ CO ₃ % | NaHCO ₃ % | NaCl % | Na ₂ SO ₄ % | Clay |
|----------------|-----------------|-------|----------------------|-----------------------------------|----------------------|--------|-----------------------------------|------|
| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
| A | 0.0-0.5 | 10.28 | 1.58 | Nil | 0.79 | 0.17 | 0.31 | 21.1 |
| | 0.5-1.0 | 10.21 | 0.90 | Nil | 0.65 | 0.19 | 0.10 | 22.8 |
| | 1.0-2.0 | 10.20 | 0.96 | Nil | 0.72 | 0.17 | 0.12 | 22.4 |
| | 2.0-3.0 | 10.24 | 0.95 | Nil | 0.68 | 0.10 | 0.22 | 15.6 |
| | 3.0-4.0 | 10.20 | 0.95 | Nil | 0.68 | 0.10 | 0.21 | 15.9 |
| | 4.0-5.0 | 10.05 | 0.59 | Nil | 0.33 | 0.10 | 0.19 | 14.5 |
| | 5.0-6.0 | 9.75 | 0.40 | Nil | 0.27 | 0.12 | 0.08 | 13.8 |
| | 6.0-7.0 | 9.45 | 0.25 | Nil | 0.20 | 0.05 | Traces | 16.0 |
| | 7.0-8.0 | 9.34 | 0.13 | Nil | 0.16 | 0.01 | do. | 9.5 |
| A ₁ | 0.0-0.5 | 9.70 | 0.34 | 0.02 | 0.18 | 0.04 | 0.09 | 17.9 |
| | 0.5-1.0 | 9.64 | 0.36 | 0.02 | 0.19 | 0.03 | 0.08 | 19.9 |
| | 1.0-2.0 | 9.82 | 0.36 | 0.07 | 0.24 | 0.03 | 0.07 | 17.2 |
| | 2.0-3.0 | 9.83 | 0.30 | 0.04 | 0.25 | 0.01 | 0.04 | 14.0 |
| | 3.0-4.0 | 9.61 | 0.18 | Nil | 0.18 | 0.02 | Nil | 14.8 |
| | 4.0-5.0 | 9.30 | 0.17 | Nil | 0.18 | 0.01 | Nil | 15.8 |
| | 5.0-6.0 | 9.14 | 0.16 | Nil | 0.18 | 0.03 | Nil | 12.0 |
| | 6.0-7.0 | 9.10 | 0.14 | Nil | 0.15 | 0.03 | Nil | 10.5 |
| | 7.0-8.0 | 9.48 | 0.11 | Nil | 0.11 | 0.01 | Nil | 7.7 |

TABLE VI (Contd.)

| Sub-Plot No. | Depth (in feet) | pH | Total soluble salt% | Na ₂ CO ₃ % | NaHCO ₃ % | NaCl % | Na ₂ SO ₄ % | Clay |
|----------------|-----------------|-------|---------------------|-----------------------------------|----------------------|--------|-----------------------------------|-------|
| 1 | 2 | 3 | 4 | 4 | 6 | 7 | 8 | 9 |
| B | 0.0-0.5 | 10.08 | 0.65 | Nil | 0.50 | 0.15 | 0.05 | 15.9 |
| | 0.5-1.0 | 10.20 | 0.60 | Nil | 0.38 | 0.17 | 0.10 | 15.8 |
| | 1.0-2.0 | 10.22 | 0.70 | Nil | 0.53 | 0.08 | 0.08 | 15.0 |
| | 2.0-3.0 | 10.24 | 0.55 | Nil | 0.38 | 0.12 | 0.07 | 11.4 |
| | 3.0-4.0 | 10.00 | 0.33 | Nil | 0.23 | 0.06 | 0.06 | 13.0 |
| | 4.0-5.0 | 9.82 | 0.40 | Nil | 0.25 | 0.12 | 0.04 | 17.8 |
| | 5.0-6.0 | 9.32 | 0.24 | Nil | 0.19 | 0.08 | Traces | 12.1 |
| | 6.0-7.0 | 9.21 | 0.17 | Nil | 0.15 | 0.05 | do. | 10.05 |
| | 7.0-8.0 | 9.44 | 0.15 | Nil | 0.16 | 0.05 | do. | 7.0 |
| B ₁ | 0.0-0.5 | 9.64 | 0.24 | Nil | 0.26 | 0.01 | Traces | 16.3 |
| | 0.5-1.0 | 9.82 | 0.31 | Nil | 0.29 | 0.02 | do. | 19.3 |
| | 1.0-2.0 | 9.88 | 0.33 | Nil | 0.35 | 0.04 | 0.02 | 17.1 |
| | 2.0-3.0 | 9.94 | 0.52 | Nil | 0.36 | 0.04 | 0.12 | 14.7 |
| | 3.0-4.0 | 9.88 | 0.41 | Nil | 0.37 | 0.06 | 0.02 | 15.9 |
| | 4.0-5.0 | 9.83 | 0.55 | Nil | 0.43 | 0.06 | 0.04 | 14.8 |
| | 5.0-6.0 | 9.66 | 0.50 | Nil | 0.32 | 0.12 | 0.09 | 11.1 |
| | 6.0-7.0 | 9.47 | 0.34 | Nil | 0.20 | 0.06 | 0.06 | 10.3 |
| C | 0.0-0.5 | 9.82 | 0.46 | Nil | 0.19 | 0.11 | 0.12 | 13.1 |
| | 0.5-1.0 | 9.85 | 0.46 | Nil | 0.29 | 0.12 | 0.06 | 13.3 |
| | 1.0-2.0 | 9.98 | 0.59 | Nil | 0.29 | 0.15 | 0.15 | 16.4 |
| | 2.0-3.0 | 9.82 | 0.70 | Nil | 0.26 | 0.16 | 0.30 | 13.0 |
| | 3.0-4.0 | 9.91 | 0.85 | Nil | 0.27 | 0.20 | 0.35 | 18.8 |
| | 4.0-5.0 | 9.98 | 0.61 | Nil | 0.35 | 0.19 | 0.08 | 15.6 |
| | 5.0-6.0 | 9.90 | 0.46 | Nil | 0.38 | 0.16 | 0.01 | 10.8 |
| | 6.0-7.0 | 9.84 | 0.27 | Nil | 0.18 | 0.05 | 0.05 | 9.8 |
| | 7.0-8.0 | 10.28 | 0.24 | Nil | 0.18 | 0.04 | 0.03 | 6.9 |

TABLE VI (Contd.)

| Sub-Plot No. | Depth (in feet) | pH | Total soluble salt% | Na ₂ CO ₃ % | NaHCO ₃ % | NaCl % | Na ₂ SO ₄ % | Clay |
|----------------|-----------------|-------|---------------------|-----------------------------------|----------------------|--------|-----------------------------------|------|
| 1 | 2 | 3 | 4 | 4 | 6 | 7 | 8 | 9 |
| C ₁ | 0.0-0.5 | 9.5 | 0.35 | Nil | 0.37 | 0.05 | Traces | 16.9 |
| | 0.5-1.0 | 9.5 | 0.32 | Nil | 0.33 | 0.03 | do. | 20.3 |
| | 1.0-2.0 | 9.2 | 0.34 | Nil | 0.36 | 0.03 | do. | 16.7 |
| | 2.0-3.0 | 9.2 | 0.44 | Nil | 0.45 | 0.05 | do. | 18.3 |
| | 3.0-4.0 | 9.2 | 0.47 | Nil | 0.37 | 0.04 | do. | 17.1 |
| | 4.0-5.0 | 9.0 | 0.35 | Nil | 0.18 | 0.12 | do. | 18.1 |
| | 5.0-6.0 | 9.2 | 0.24 | Nil | 0.15 | 0.08 | do. | 11.7 |
| | 6.0-7.0 | 9.2 | 0.22 | Nil | 0.15 | 0.09 | do. | 8.0 |
| | 7.0-8.0 | 9.2 | 0.18 | Nil | 0.18 | 0.05 | do. | 5.7 |
| D | 0.0-0.5 | 9.92 | 0.64 | Nil | 0.39 | 0.10 | 0.13 | 19.1 |
| | 0.5-1.0 | 10.40 | 0.55 | Nil | 0.23 | 0.09 | 0.20 | 18.6 |
| | 1.0-2.0 | 10.12 | 0.57 | 0.16 | 0.26 | 0.10 | 0.07 | 16.6 |
| | 2.0-3.0 | 9.94 | 0.46 | 0.16 | 0.20 | 0.08 | 0.02 | 13.5 |
| | 3.0-4.0 | 9.90 | 0.41 | Nil | 0.26 | 0.06 | 0.09 | 18.3 |
| | 4.0-5.0 | 9.89 | 0.38 | Nil | 0.27 | 0.07 | 0.06 | 13.7 |
| | 5.0-6.0 | 9.80 | 0.28 | Nil | 0.22 | 0.06 | 0.02 | 12.9 |
| | 6.0-7.0 | 9.68 | 0.25 | 0.04 | 0.18 | 0.06 | 0.02 | 8.3 |
| | 7.0-8.0 | 9.71 | 0.24 | Nil | 0.18 | 0.06 | 0.01 | 7.5 |
| D ₁ | 0.0-0.5 | 9.5 | 0.24 | Nil | 0.22 | 0.03 | 0.02 | 16.1 |
| | 0.5-1.0 | 9.5 | 0.31 | Nil | 0.24 | 0.06 | 0.03 | 18.0 |
| | 1.0-2.0 | 9.5 | 0.49 | Nil | 0.31 | 0.15 | 0.10 | 15.9 |
| | 2.0-3.0 | 9.5 | 0.70 | Nil | 0.46 | 0.15 | 0.03 | 15.3 |
| | 3.0-4.0 | 9.0 | 0.55 | Nil | 0.20 | 0.09 | 0.16 | 16.6 |
| | 4.0-5.0 | 9.0 | 0.31 | Nil | 0.28 | 0.03 | Traces | 17.7 |
| | 5.0-6.0 | 9.0 | 0.16 | Nil | 0.14 | 0.05 | do. | 12.0 |
| | 6.0-7.0 | 9.2 | 0.14 | Nil | 0.14 | 0.03 | do. | 9.5 |
| | 7.0-8.0 | 9.2 | 0.16 | Nil | 0.13 | 0.05 | do. | 7.6 |

Berseem is leguminous and enriches the soil. From the present results it was inferred that the soils having pH values of about 9.5 could be conveniently reclaimed by putting in a rotation of Berseem. But it is a winter crop and needs sufficient water-supply for its maturity. Therefore its use will have to depend upon the availability of irrigation water in winter.

SUMMARY

The following main conclusions were drawn from the analytical results of soil samples taken before and after reclamation operations of alkali plots, subjected to the different types of crop rotations:

- (a) Leaching-jantar, (*Sesbania aculeata*)-fallow-jantar (green manuring).
- (b) Sugarcane-(Ratooned).
- (c) Leaching-rice-gram.
- (d) Leaching-swank (*Panicum colonum*)-Berseem (*Trifolium alexandrinum*).
- (i) The most efficient crop rotation for the reclamation of alkali soils is green manuring with jantar (*Sesbania aculeata*). Its ameliorative effect had been observed even at 5' depth.
- (ii) Rice followed by gram comes next to jantar (*Sesbania aculeata*).
- (iii) The rotation of Swank (*Panicum colonum*) followed by Berseem may be recommended for the reclamation of alkali soils having pH value not above 9.5.
- (iv) Sugarcane may stand sufficiently high degree of alkalinity, even about 9.5 pH, but it does not help much in reducing the alkalinity of soils.

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CHEMICAL EXAMINATION OF *MATTHIOLA* *INCANA* (YELLOW VARIETY)

Part I. Study on Oil

BY D. S. BHAKUNI AND B. C. JOSHI

[Chemical Laboratories, University of Allahabad, Allahabad (India)]

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Matthiola incana R.Br. H.F.B.I. (yellow variety), also known as *Lipedium iberis*, Hindi-Pili Todri, belonging to N.O. *Cruciferae* is cultivated in Indian gardens, indigenous to mediterranean regions and Western Europe. It also extends from Southern Europe to Siberia. It is a well known medicinal plant and is used by Ayurvedic physicians as aphrodisiac and in purifying blood. The Uanni physicians have prescribed the seeds in cancer; with wine they are given as an antidote to poisonous bites but are not antidote to snake venoms.

Matthiola incana seeds (yellow variety) have been subjected to a systematic chemical examination. The seed was tested for both organic and inorganic substances. On complete incineration, the powdered seeds gave 10.2% of greyish white ash of which 43.4% was water-soluble and rest was acid-soluble. The ash on analysis was found to contain sodium, potassium, aluminium, iron, calcium and magnesium as basic radicals and chloride, sulphate, carbonate, silicate and phosphate as acid radicals.

Preliminary chemical examination of the seeds showed the presence of an oil, mucilage and a mixture of colouring matters. The alkaloids, glucosides, saponins, reducing sugars and free organic acids were found to be absent.

The complete chemical study of the oil revealed that erucic (37.60%), oleic (19.89%) and linoleic acids (32.52%) were present as major components, a characteristic of the oils obtained from *Cruciferous* seeds while palmitic (2.24%), stearic (2.86%) and linolenic acids (4.86%) were present as minor components in the mixed acid fraction. The unsaponifiable matter consists of phytosterols and β -sitosterol.

EXPERIMENTAL

Chemical examination of the oil

Extraction and purification.—Three and a half kilograms of powdered seed were exhaustively extracted with petroleum ether (b.p. 40–60° C.). The petroleum ether extract was filtered hot and kept overnight. No solid substance settled down on keeping. From the petroleum ether extract the crude oil was obtained and purified (Yield = 7.92%).

The following physical and chemical constants of the pure oil were determined (Table I).

Two hundred and twenty gms. of the oil were saponified with an alcoholic solution of potassium hydroxide; alcohol was distilled off and the unsaponifiable matter (0.82%) was removed with ether. The soap solution was then decomposed

TABLE I

| Constants | Values |
|---------------------------|-----------|
| Iodine value (Hanus) | .. 112.3 |
| Saponification value | .. 184.2 |
| Acid value | .. 20.1 |
| Refractive index | .. 1.4301 |
| Specific gravity (30° C.) | .. 0.9221 |
| Unsaponifiable matter | .. 0.82% |

with dilute sulphuric acid and the fatty acids (80.2%) were obtained by ether extraction. The mixed fatty acids were then separated into solid and liquid acids by the Twitchell's lead salt alcoholic process modified by Hilditch and co-workers.¹ The percentage and chemical constants of the solid and liquid acid fractions are given in Table II.

TABLE II

| Fraction | Percentage | Iodine value |
|-------------------------|------------|--------------|
| 1. Solid acid fraction | 18.46 | 58.2 |
| 2. Liquid acid fraction | 81.53 | 134.2 |

Quantitative estimation of liquid acids.—The estimation of the liquid acids was carried out by two methods, bromination method and methyl-ester method.

(A) *Bromination method*

Ten gms. of the acid from the liquid acid fractions were estimated by dissolving the acid in ether (at -10° C.) and brominated according to the method of Eibner and Muggenthaler² modified by Jamieson and Boughmann.³ The results are given in Table III.

TABLE III

| Sl. No. | Acids | Percentage in mixed acid |
|---------|-----------|--------------------------|
| 1 | Oleic | 16.32 |
| 2 | Linolenic | 4.87 |
| 3 | Linoleic | 32.51 |

(B) *Methyl ester method*

The percentage of liquid acids was determined by preparing their methyl esters and distilling a known quantity of the esters under reduced pressure (10 mm.). Different fractions were collected, iodine and saponification values of each fraction were determined. From these values the amount of various acids in different fractions were calculated according to the method of Jamieson and Boughmann.⁴ The observations and results obtained are given in Table IV.

TABLE IV

(Weight of the methyl esters taken = 20.3017 gms.; Pressure = 10 mm.)

| Fraction | Temperature range | Weight in gms. | Oleic acid | Linoleic acid | Linolenic acid | Erucic acid | Solid acid |
|----------|-------------------|----------------|------------|---------------|----------------|-------------|------------|
| 1 | Upto 190° C. | 1.9989 | 1.9364 | .. | .. | .. | 0.0625 |
| 2 | 190–195° C. | 4.4668 | 2.0272 | 2.4396 | .. | .. | .. |
| 3 | 195–200° C. | 5.7750 | .. | 5.5404 | 0.2346 | .. | .. |
| 4 | 200–210° C. | 3.3033 | .. | .. | 0.9569 | 2.3464 | .. |
| 5 | Above 210° C. | 4.4577 | .. | .. | .. | 4.4577 | .. |
| TOTAL | | 20.0017 | 3.9636 | 7.9800 | 1.1915 | 6.8041 | 0.0625 |

Loss during distillation = 0.3 gms.

The results of the estimation of the acids in liquid acid fraction obtained by bromination and methyl ester methods are given in Table V.

TABLE V

| Fatty acids | Bromination method | | Methyl ester method | |
|-------------|------------------------------------|-----------------------------------|------------------------------------|-----------------------------------|
| | Percentage in liquid acid fraction | Percentage in mixed acid fraction | Percentage in liquid acid fraction | Percentage in mixed acid fraction |
| Palmitic | .. | .. | 0.31 | 0.24 |
| Oleic | 20.02 | 16.32 | 19.82 | 16.16 |
| Linolenic | 5.90 | 4.87 | 5.96 | 4.86 |
| Linoleic | 39.90 | 32.51 | 39.88 | 32.52 |
| Erucic | .. | .. | 34.02 | 27.73 |

It is clear from the above results that by bromination method erucic acid and solid acid cannot be estimated and for their estimation methyl ester method is to be employed.

Quantitative examination of the solid acids

Methyl ester method.—The solid acids were converted into their methyl esters as in the case of liquid acids. The results obtained are given in Table VI.

TABLE VI

(Weight of the methyl esters taken = 20·1200 gms.; Pressure 10 mm.)

| No. of fraction | Temperature | Weight in gms. | Palmitic acid | Stearic acid | Oleic acid | Erucic acid |
|-----------------|---------------|----------------|---------------|--------------|------------|----------------|
| 1 | 170–175° C. | 1·2034 | .. | 1·2034 | .. | .. |
| 2 | 175–180° C. | 2·4324 | 1·4674 | 0·9650 | .. | .. |
| 3 | 180–185° C. | 3·1218 | 1·6330 | .. | 1·4888 | .. |
| 4 | 185–190° C. | 4·9182 | .. | .. | 2·5536 | 2·3646 |
| 5 | Above 190° C. | 8·3234 | .. | .. | .. | 8·3234 |
| TOTAL | | .. | 19·9992 | 3·1004 | 2·1684 | 4·0424 10·6880 |

Loss during distillation=0·1308 gms.

From the results tabulated in Table VI the percentages of stearic, palmitic, oleic and erucic acids were calculated in solid and mixed acid fractions. The results obtained are given in Table VII.

TABLE VII

| Fatty acids | Percentage in solid acid fraction | Percentage in mixed acid fraction |
|---------------|-----------------------------------|-----------------------------------|
| Palmitic acid | .. 10·84 | 2·00 |
| Stearic acid | .. 15·50 | 2·86 |
| Oleic acid | .. 20·21 | 3·73 |
| Erucic acid | .. 53·44 | 9·87 |

The examination of the oil from the seeds of *Matthiola incana* revealed that the component fatty acids present in the oil are palmitic, stearic, oleic, erucic, linolenic and linoleic acids.

The results of estimation of these component fatty acids in solid acid, in liquid acid and in mixed fatty acid fractions are given in Table VIII.

TABLE VIII

| Fatty acids | | Percentage in solid acid fraction | Percentage in liquid acid fraction | Percentage in mixed acid fraction |
|-------------|----|---|--|---|
| Palmitic | .. | 10.84 | 0.31 | 2.24 |
| Stearic | .. | 15.50 | .. | 2.86 |
| Oleic | .. | 20.21 | 15.82 | 19.89 |
| Linoleic | .. | .. | 39.88 | 32.52 |
| Linolenic | .. | .. | 5.96 | 4.86 |
| Erucic | .. | 53.44 | 34.02 | 37.60 |

EXAMINATION OF UNSAPONIFIABLE MATTER

The unsaponifiable matter was obtained by extracting the soap solution with ether. It was a semi-solid yellowish brown mass, having a characteristic smell. It was purified with petroleum ether and recrystallized from alcohol. The pure product gave positive tests for sterols. It was a white crystalline compound which melted at 136–37° C. Its acetyl derivative melted at 123° C. Thus the sterol was inferred to be β -sitosterol.

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THE SILVER CATALYSED REDUCTION OF PERSULPHATE BY OXALIC ACID

BY YUGUL KISHORE GUPTA AND SATYESHWAR GHOSH

(*Chemical Laboratories, University of Allahabad, Allahabad*)

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ABSTRACT

The silver catalysed reduction of persulphate by oxalic acid has been studied under conditions exactly similar to that of potassium oxalate as reported earlier. The reaction is characterised by a long induction period, the probable cause of which is something in the oxalic acid sample itself. The reaction rate increases with the increase in the concentration of the persulphate, and slightly decreases with the increase in the concentration of oxalic acid. In presence of sulphuric acid, the reaction rate is much slower. Nitrate ion inhibits the reaction.

In a recent communication¹ we have reported that oxalic acid and normal potassium oxalate react differently with the persulphate. The above paper contains the investigations on the silver catalysed reduction of persulphate by potassium oxalate in sulphuric acid medium, wherein the reaction was found to be of first order without any induction period or autocatalytic curve. In presence of sulphuric acid, the oxidation of oxalic acid should be very similar to the oxidation of potassium oxalate in presence of sulphuric acid and theoretically there should be no induction period with oxalic acid also, as with potassium oxalate because the reacting species are the same in both the cases. The results of the present investigation, however, show that the reaction is characterised by a long induction period, followed by a very fast reaction and then auto-inhibition as was found by King,² Allen³ and Srivastava and Ghosh⁴ in the uncatalysed reaction. It was, therefore, considered necessary and interesting to make a thorough investigation with oxalic acid for a possible explanation of this anomalous behaviour. Oxidation of oxalic acid was carried out in presence of silver ions and the kinetics were followed by estimating the persulphate iodometrically by the recommended method of Szabo, Csanyi and Galiba,⁵ which is simpler than the method of Barlett and Cotman⁶ adopted by Allen³ for studying the kinetics.

EXPERIMENTAL

The medium of reaction was redistilled water from a quartz vessel. All the vessels used for storing stock solutions or redistilled water, pipettes, measuring flasks and reaction vessel itself, were of jena glass and the latter was coated outside with black japan to exclude photochemical effect, if any.

All the chemicals used were either of B.D.H., A.R. or of E. Merck, G. R. quality. Sulphuric acid was of Basynth, A.R., quality (specific gravity 1.84).

Stock solutions of oxalic acid and silver nitrate were made. Persulphate solution was always freshly prepared and its concentration checked by arsenite⁷

or by ferrous sulphate method.⁸ All other solutions were prepared in the usual way.

Calculated quantity of oxalic acid and potassium persulphate were taken in the reaction vessel and placed in a thermostat at 34° C. Silver nitrate solution was kept separately. When the reactants had attained the required temperature, a known amount of silver nitrate was transferred to the reaction vessel by means of a pipette. 5 ml. of the reaction mixture were taken out at different intervals of time, in a beaker containing 2.5 ml. of 60% potassium iodide, 2.5 ml. of concentrated hydrochloric acid and 1 ml. of the catalyst. The catalyst was prepared by dissolving 2.59 gm. of A.R. ferrous ammonium sulphate and 9.82 gm. of A.R. copper sulphate in 500 ml. of distilled water. A drop or two of concentrated sulphuric acid was added to make the solution clear. In this method of estimation, use of marble pieces has been recommended by Szabo, Csanyi and Galiba,⁵ but we did not use them as no significant improvement was made by their use as observed separately. Hydrochloric acid checked the reaction by precipitating silver as chloride and also by direct inhibition. Chloride ions have been found to inhibit the uncatalysed reaction as reported by Srivastava and Ghosh.⁹ Unreacted persulphate and copper sulphate liberated iodine which was titrated against 0.04 N sodium thiosulphate from a microburette. A blank was also run with the catalyst and all other reactants except the persulphate, and the blank was subtracted from the reading of the microburette.

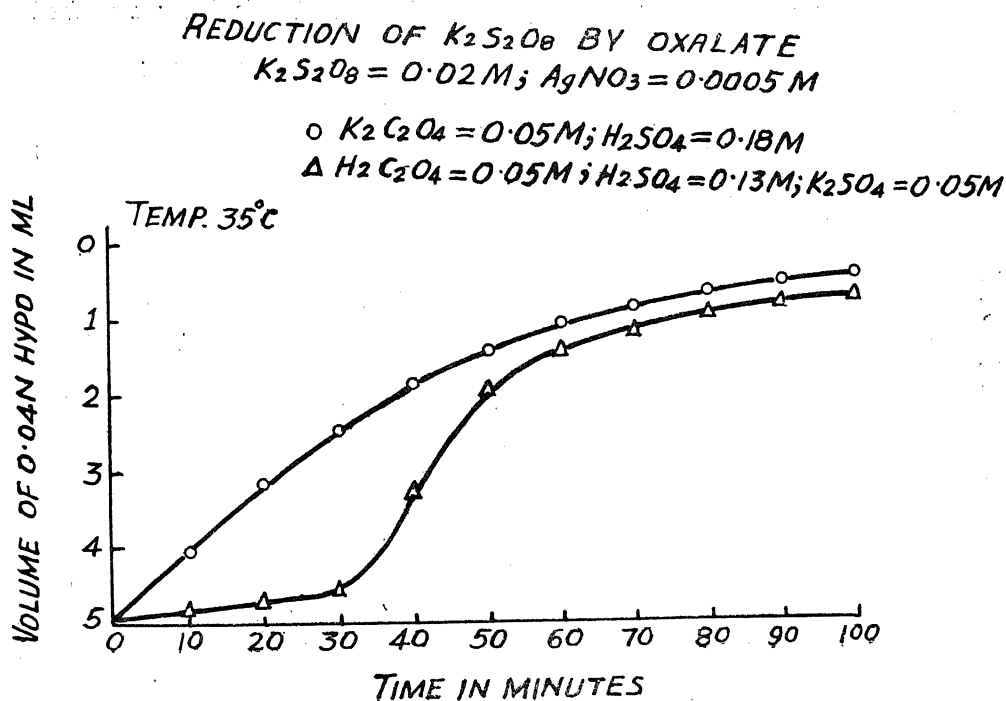


FIG. 1

RESULTS

Figure 1 gives the results of two experiments with exactly similar concentrations of all the reacting species, but in one experiment potassium oxalate was used while in the other, oxalic acid was employed.

It will be seen that potassium oxalate and oxalic acid react differently and that the induction period is still a characteristic with the oxalic acid. Allen³ attributes dissolved oxygen to be the cause of this induction period. This argument is difficult to accept because the experiments were performed with freshly boiled and cooled redistilled water and no induction period is observable in the reaction with potassium oxalate, hence there is no reason why dissolved oxygen should not produce an induction period in the reaction with potassium oxalate also, if this explanation were sound. Srivastava and Ghosh⁴ have reported that it is due to the want of hydrogen ions. We studied the reaction also in presence of varying amounts of sulphuric acid and found (Fig. 2) that the induction period on the contrary, increases with the increasing concentration of sulphuric acid, so much so that in presence of 1.8 M H_2SO_4 the reaction is appreciably slow. King,² however, is of the opinion that the formation of some intermediate complex is the cause of the induction period. This could neither be confirmed nor disproved by us. We are led to believe that there is something in oxalic acid sample itself which is responsible for the induction period.

It is interesting to find that the silver catalysed oxidation of oxalic acid by persulphate is slow in presence of sulphuric acid, although this forms a method

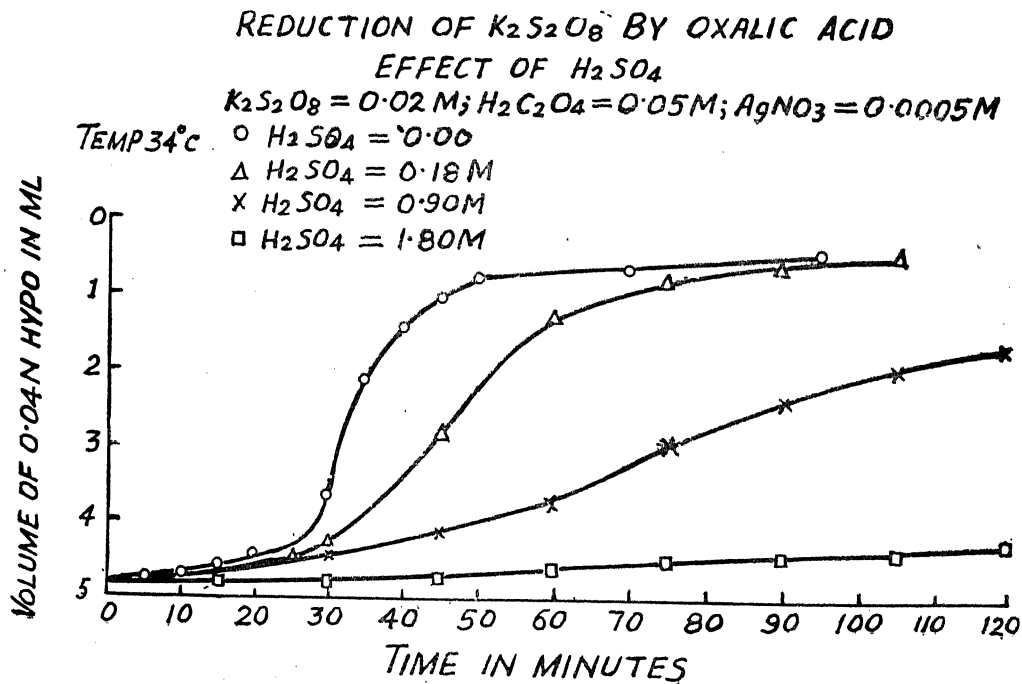


FIG. 2

REDUCTION OF $K_2S_2O_8$ BY OXALIC ACID
DIFFERENT CONCENTRATIONS OF $H_2C_2O_4$

$K_2S_2O_8 = 0.02M$; $AgNO_3 = 0.0005M$

$\Delta H_2C_2O_4 = 0.1M$

$\circ H_2C_2O_4 = 0.05M$

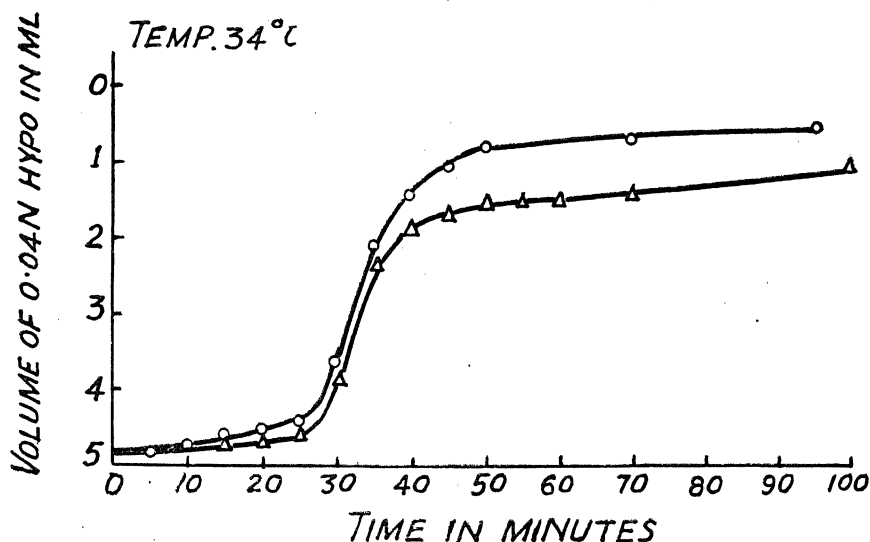


FIG. 3

for the quantitative estimation¹⁰ of persulphate. This apparent anomaly is because in the method used in analysis, the silver concentration used is 400–500 times than that employed in this investigation, and the reaction mixture is heated on a water-bath for 15–20 minutes.

Figures 3 and 4 give the effect of varying concentrations of persulphate and of oxalic acid on the rate of the reaction. It may be seen that the induction period decreases and the reaction becomes faster with increase in the concentration of the persulphate. Increase in the concentration of oxalic acid, slightly lowers the rate of the reaction as has been reported by Srivastava and Ghosh in the oxidations of formic acid¹¹ and of oxalic acid.⁴

Effects of potassium sulphate, potassium nitrate and magnesium sulphate on the reaction, were also seen. Figure 5 shows these results. Potassium sulphate is very similar in action to sulphuric acid. Magnesium sulphate has slightly less depressing influence than potassium sulphate. Potassium nitrate lowers the rate to a great extent. It appears that in the oxidation of oxalic acid also, the ions

REDUCTION OF $K_2S_2O_8$ BY OXALIC ACID
DIFFERENT CONCENTRATIONS OF $K_2S_2O_8$

$H_2C_2O_4 = 0.05M$; $AgNO_3 = 0.0005M$

○ $K_2S_2O_8 = 0.04M$

△ $K_2S_2O_8 = 0.02M$

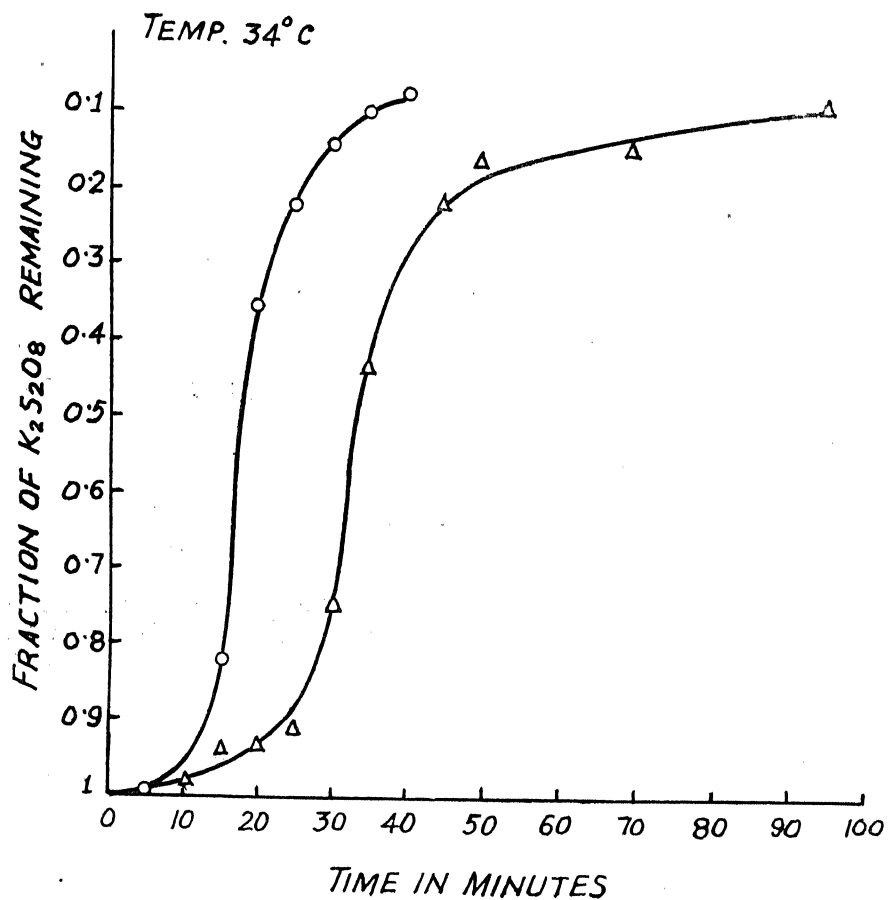


FIG. 4

have some specific influence. Nitrate ion seems to inhibit the reaction as in the case of potassium oxalate.¹

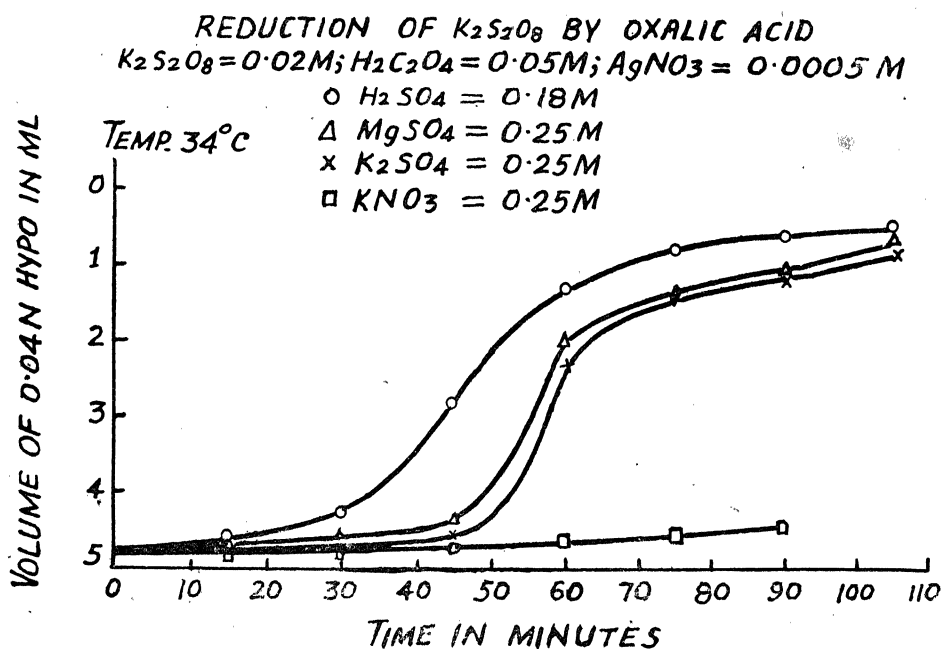


FIG. 5

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